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THE

PHYSICAL REVIEW.

THE EFFECT OF TENSION ON THE CHANGE OF THERMOELECTROMOTIVE FORCES BY MAGNETIZATION.

By Alpheus W. Smith.

Synopsis.

Combined Effect of Tension and Magnetic Field on Thermoelectromotive Force and Resistance of Some Ferro-magnetic Metals.—Wires 10 cm. long and 0.15 cm. in diameter were each held in heavy brass clamps and stretched while placed axially in a vertical solenoid. While determining the electromotive forces, one end was kept at 100°, the other at 0° C. In the case of *nickel*, the effect of tension on the change in resistance (ΔX) and in thermoelectromotive force (ΔE) produced by a longitudinal magnetic field is a decrease for weak fields but an increase for larger fields. For a given tension, the ratios of ΔX to ΔE and to the magnetic change of length (ΔL) are independent of the field strength and therefore seem to depend on the same factor. *Pure iron* shows a parallelism between the effects of tension on ΔE and ΔL; with increasing tension the curves for ΔE as function of the field shift downward so that for sufficiently large tensions ΔE becomes negative throughout. The curve for ΔE may be considered the sum of two effects, associated with two forms of iron, one of which is proportional to ΔL and is affected by tension more than the other. The behavior of *iron-copper alloys* is qualitatively similar to that of iron. *Iron-nickel alloys* behave like iron until the per cent. of Ni is more than 7 when they tend to behave more and more like Ni. For both series of alloys the change of ΔX due to tension is always a decrease.

Relation between the Hall Constant, Specific Resistance and Fractional Change of Thermoelectromotive Force Produced by a Magnetic Field in a Series of Iron-copper Alloys is pointed out. The three properties vary with copper content in a similar way, all showing a cusp for 1.5 per cent. copper.

Electron Theory of Conductivity and Thermoelectromotive Force.—In a *discussion* of the above results it is shown that neither the gas-free theory as given by Heaps nor Bridgman's gap theory explains them satisfactorily. The decrease in resistance with increase of length would be expected, however, if the number of free electrons varies in an inverse manner with the atomic frequency; and ΔE would vary with magnetic field and tension if the atomic frequency and the number of free electrons are not the same functions of the magnetic field at different temperatures and tensions.

THE influence of tension on the resistance, length, permeability and elastic constants of ferromagnetic substances in longitudinal magnetic fields has been frequently studied. Similar observations do

not seem to have been made on the effect of tension on the changes in the thermoelectromotive forces produced by such a magnetic field. In view of the dependence of the resistance and the thermoelectromotive force on each other and on the elastic and magnetic properties of the substance, it seemed of interest to study the variation of the thermoelectromotive forces produced by a longitudinal magnetic field when the substances were sustaining tensions of different amounts.

Methods of Observation.—The specimens to be studied were in the form of thin wires about 10 cms. in length and .15 cm. in diameter. These wires after being fastened to heavy brass rods were suspended axially in a solenoid which was 40 cms. long. The wires lay near the center of the solenoid where the magnetic field was nearly uniform. At a point just below or above the junction of the brass rods and the wires there was soldered a copper wire which with the specimen formed a thermal couple. One junction was kept in a mixture of ice and water and the other in steam at atmospheric pressure. The tensions were applied to the specimens by placing different weights on a scale pan suspended from the wire.

The thermoelectromotive force arising from the couple was nearly balanced by connecting the copper lead wires in the usual manner to a Wolff potentiometer. The thermoelectromotive forces set up by the longitudinal magnetic field were determined by noting the deflection of a sensitive Leeds and Northrup galvanometer of the d'Arsonval type. From this deflection together with the sensibility of the galvanometer the change in thermoelectromotive force produced by the longitudinal magnetic field was calculated. The total electromotive force of the couple was read directly from the potentiometer.

In order to compare the effect of tension on the change of thermoelectromotive force with the effect of tension on the longitudinal change of resistance, some observations were made on the change of resistance in a magnetic field in these same wires when the wires were sustaining loads of different amounts. The measurements of the changes of resistance were made by means of a Kelvin double bridge. The bridge was balanced as nearly as possible when there was no magnetic field in the solenoid. The deflection of the galvanometer resulting from the establishment of the magnetic field in the solenoid gives a measure of the change of resistance in the specimen resulting from the action of the magnetic field. To calculate the change of resistance from this deflection it is necessary to know the current in the specimen and the sensitivity of the galvanometer besides the resistances entering into the network of the bridge. For resistances of the magnitude used in these

experiments the change of resistance can be calculated with sufficient accuracy from the formula,[1]

$$\frac{\Delta X}{X} = \frac{K}{PI_b}\left[R_g \left(1 + \frac{N}{M} \right) + 2N \right] D,$$

where
K = current to produce 1 cm. deflection,
D = deflection of galvanometer in cms.,
R_g = resistance of galvanometer,
I_b = current in the unknown resistance,
N, M and P = resistances in the arms of bridge.

Besides nickel and iron a number of alloys of iron and copper and also some alloys of nickel and iron were studied. These are the same alloys which were used by the author in a study of the Hall effect and the Nernst effect.[2] They were prepared by Burgess and Aston[3] from exceptionally pure metals. The observations on the change of resistance were made at room temperature. The changes in the thermoelectromotive forces are the changes which arise when one junction is at 0° C. and the other at 100° C. The tensions which have been recorded on the following curves have been expressed in kilograms per sq. mm.

The curves in Fig. 1 show the change of resistance and the change of

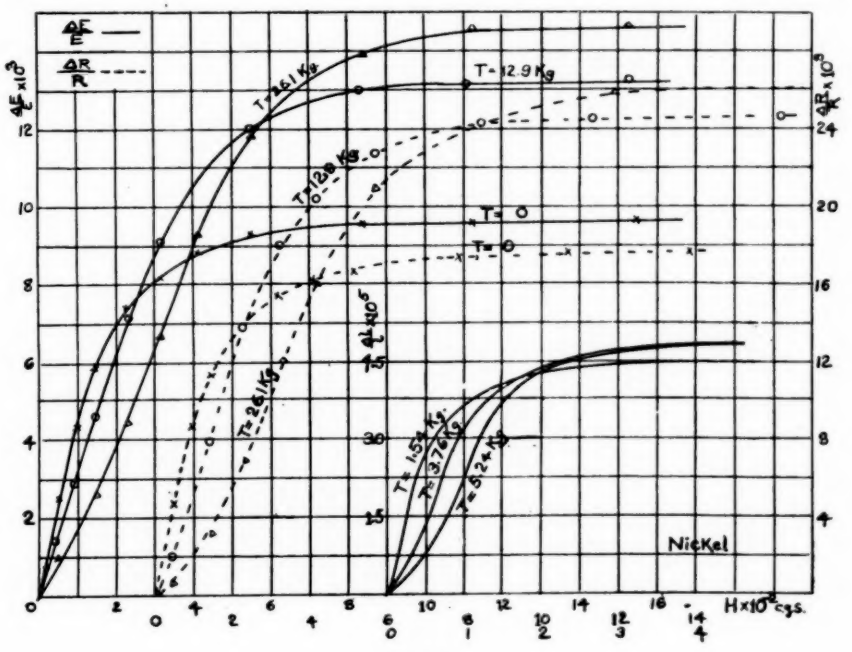

Fig. 1.

[1] Laws, Electrical Measurements, p. 194.
[2] Smith, PHYS. REV. (2), 17, 23, 1921.
[3] Burgess and Aston, Met. and Chem. Eng., 8, 19, 1910.

thermoelectromotive force in nickel under different loads in a longitudinal magnetic field. This nickel was of unknown purity. It was obtained from Eimer and Amend as pure nickel. For the sake of comparison there has been plotted in this same figure the fractional change of length in nickel in a longitudinal magnetic field. The data for these curves were taken from the work of Honda and Terada.[1] These curves have been plotted above the horizontal axis without regard to the sign of the effect whether positive or negative. The magnetic field produces an increase in the resistance, a decrease in the thermoelectric height against copper and a decrease in length. An examination of these curves shows that the change in thermoelectromotive forces produced by a longitudinal magnetic field behave in almost exactly the same way in which the change of resistance and the change of length behave. The effect of tension is to decrease the effect of the magnetic field on the resistance, length and thermoelectromotive forces for smaller magnetic fields. On

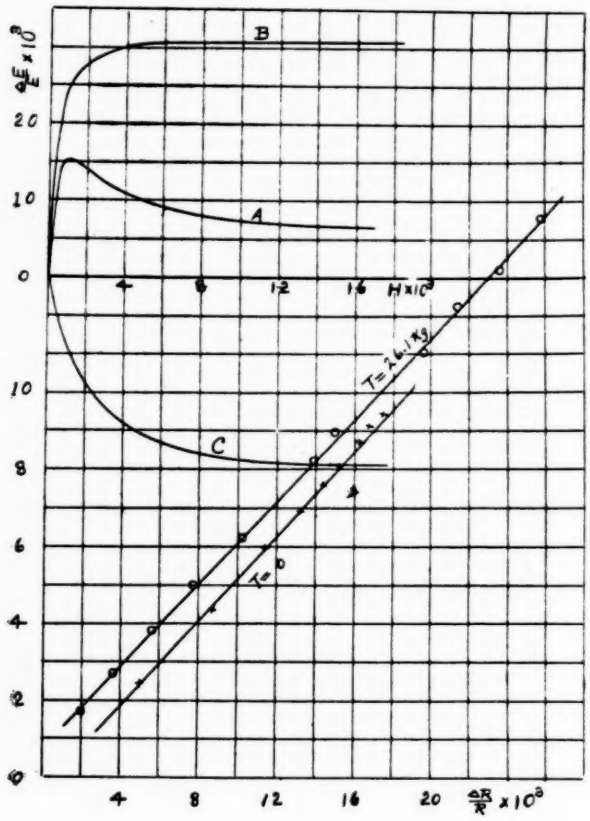

Fig. 2.

[1] Honda and Terada, Phil. Mag. (6), 13, 36, 1907.

the other hand for the larger magnetic fields these changes are greater for large tensions than for small tensions.

In the lower half of Fig. 2 the fractional change of resistance for a particular magnetic field has been plotted against the fractional change of thermoelectromotive force, for the case in which the wire is unloaded and for the case in which the wire sustains the maximum load. A proportionality is found between these two changes. The factor of proportionality is a function of the tension. Heaps[1] has pointed out that there is in nickel a proportionality, except for small magnetic fields, between the change of resistance and the change of length. To these observations is added the fact that in nickel the change in thermoelectromotive force is proportional to both the change of resistance and the change of length. From this it is clear that whatever factors determine the change of length of nickel, in much the same way they determine the change of resistance and the change of thermoelectromotive force. Grondall,[2] however, failed to find a simple relation between the change in length and the change in thermoelectromotive forces in Heusler alloys.

Similar observations on pure iron show a parallelism between the change of thermoelectromotive force produced by the magnetic field when the wire sustains different loads and the change in length under corresponding conditions. The curves at the bottom of Fig. 3 are taken

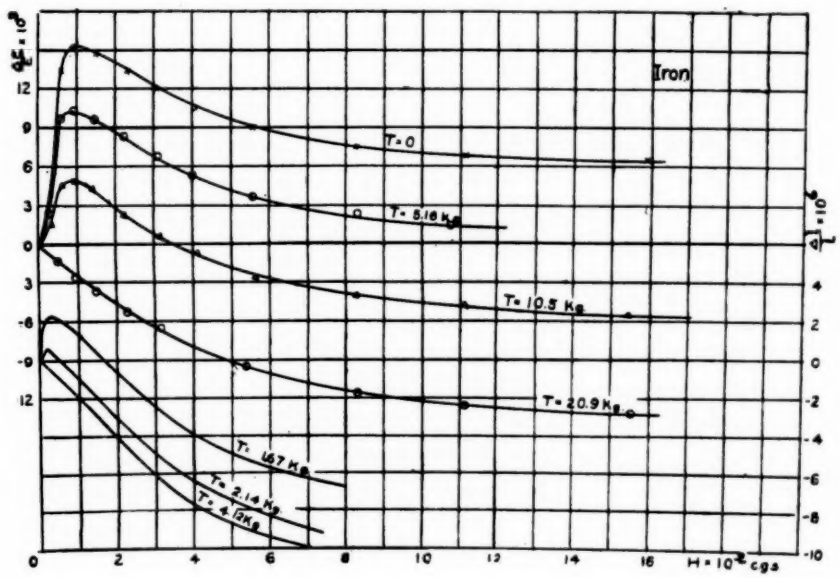

Fig. 3.

[1] Heaps, PHYS. REV. (2), 6, 34, 1915.

[2] Grondall, PHYS. REV. (2), 4, 325, 1914.

from the work of Honda and Terada. A comparison of these curves with those above them shows that the effect of tension on the change of length in a magnetic field and its effect on the change in the thermoelectromotive force are quite similar. In each case the application of tension decreases the initial effect. When the tension is sufficiently large the direction of the change is reversed. The initial change of the length is an elongation and this at sufficiently large fields and tensions becomes a contraction. The initial change in the thermoelectromotive force is an increase in the thermoelectric power with respect to copper. For sufficiently large magnetic fields and tensions this reverses and becomes a decrease. An increase in length is associated with increase in thermoelectric power. The larger the tension the smaller the magnetic field at which this reversal takes place. The reversal of the direction of the change of length takes place for smaller tensions and smaller magnetic fields than those necessary for the reversal of the direction of the change of thermoelectromotive force. This may be due to the fact that the two changes were not studied in the same specimen of iron. For sufficiently large tensions the curve starts downward from the origin and the change of length is always a contraction and the thermoelectric power is always decreased.

The linear relation between the change of length, resistance and thermoelectromotive force found in the case of nickel does not hold in the case of iron. The curves (Fig. 9) showing the relation between the change of resistance and the magnetic field have the usual form for iron. The application of tension causes a decrease in the change of resistance produced by the magnetic action. In nickel tension caused a decrease in the change of resistance which was later followed by an increase at sufficiently large magnetic fields. Heaps[1] found a proportionality between the change of length and the change of resistance in a longitudinal magnetic field. The curve which he gives to show the relation between the change of length and the magnetic field is very different from those given by other observers except for one case recorded by Bidwell.[2] The reason for the discrepancies between the observations of Heaps and those of other observers is not evident, unless it be due to polymorphism of iron and in one of these forms the change is positive and in the other it is negative.

Now each of these curves showing the relation between the change of length and the change of thermoelectric power in iron in a longitudinal magnetic field can be arbitrarily broken up into two parts as shown in the upper half of Fig. 2. This is equivalent to regarding the magneto-

[1] Heaps, PHYS. REV. (2), 6, 34, 1915.

[2] Bidwell, Proc. Roy. Soc., 56, 1894.

strictive effect as well as the change in thermoelectric power as made up of two parts, one positive and the other negative. One of these parts is represented by Curve *B* and the other by Curve *C*.

The sum of the ordinates of Curve *B* and Curve *C* gives the ordinates of the observed Curve *A*. If this analysis is correct it may be that for some reason the part of the total effect represented by Curve *B* was negligible in the specimen studied by Heaps. In view of the polymorphic character of iron this is not improbable. This would leave the curve *C* which corresponds to his observations. If such a splitting up of the effects into two parts is allowable it may be that there is still a proportionality between the change of resistance and one of the terms entering into the observed change of length and thermoelectromotive force. This analysis is the more probable in view of the effect of tension on the change of length and on the change of resistance. This effect of tension might be interpreted as decreasing that part of the effect represented by Curve *B* and leaving the second part essentially unchanged. When the tension was made large enough, a reversal of the change would then follow for sufficiently large magnetic fields. It would also follow that the larger the tension the smaller the magnetic field necessary to reverse the effect. If the tension were made large enough to render the first part of the effect represented by Curve *B* negligible in comparison with the second part represented by Curve *C*, the change of length and the change of thermoelectromotive force would always have the same sign and might be represented by the observed curves as found for large values of the tension.

In Figs. 4, 5, 6, 7 and 8 are given curves showing the change in the thermoelectromotive force as a function of the magnetic field for six alloys of iron and copper and three alloys of iron and nickel. All of these curves except those for the alloy containing 93 per cent. iron and 7 per cent. nickel and the alloy containing 88.7 per cent. iron and 11.3 per cent. nickel have the characteristics of the corresponding curves for pure iron. The addition of copper to iron changes the magnitude of the effect of a given longitudinal magnetic field on the thermoelectric power but in other respects the behavior of the alloys is very similar to the behavior of the iron. The direction of the thermoelectromotive force and also the direction of its change in the magnetic field is the same in these alloys as in pure iron. The addition of copper to iron at first increases the effect of the longitudinal magnetic field on the thermoelectromotive force. After the alloy contains 1.5 per cent. copper a further increase in the concentration of copper decreases the change in thermoelectromotive force.

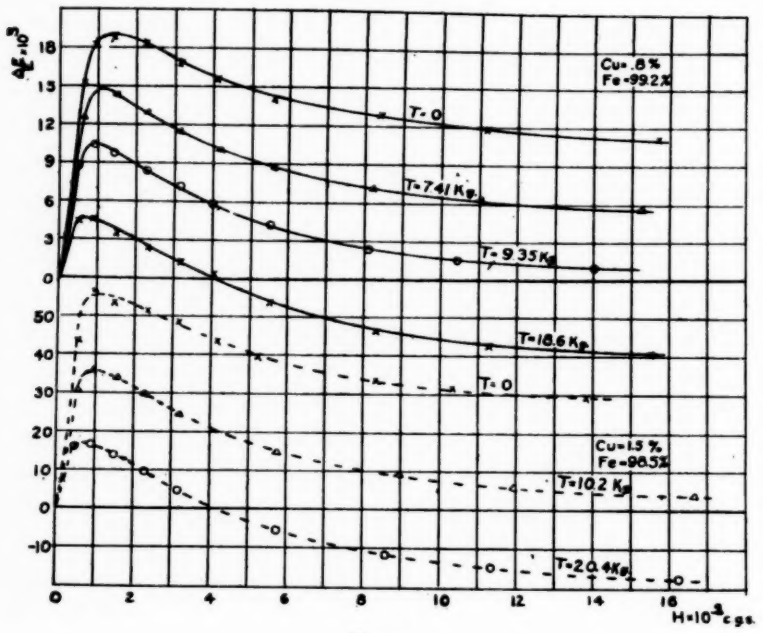
Cu=.6%
Fe=99.2%
T=0
T=7.41 Kg.
T=9.35 Kg.
T=18.6 Kg.
T=0
Cu=1.5%
Fe=98.5%
T=10.2 Kg.
T=20.4 Kg.
H×10⁻³ c.g.s.

Fig. 4.

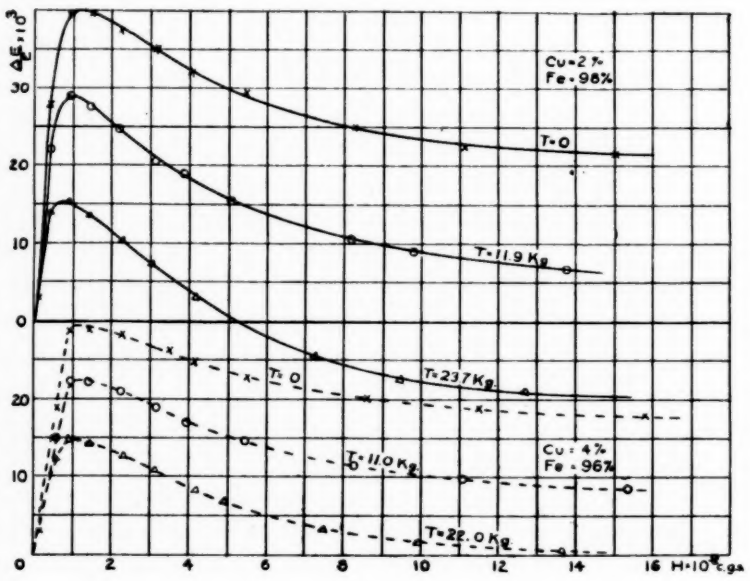
Cu=2%
Fe=98%
T=0
T=11.9 Kg.
T=23.7 Kg.
T=0
T=11.0 Kg.
Cu=4%
Fe=96%
T=22.0 Kg.
H×10⁻³ c.g.s.

Fig. 5.

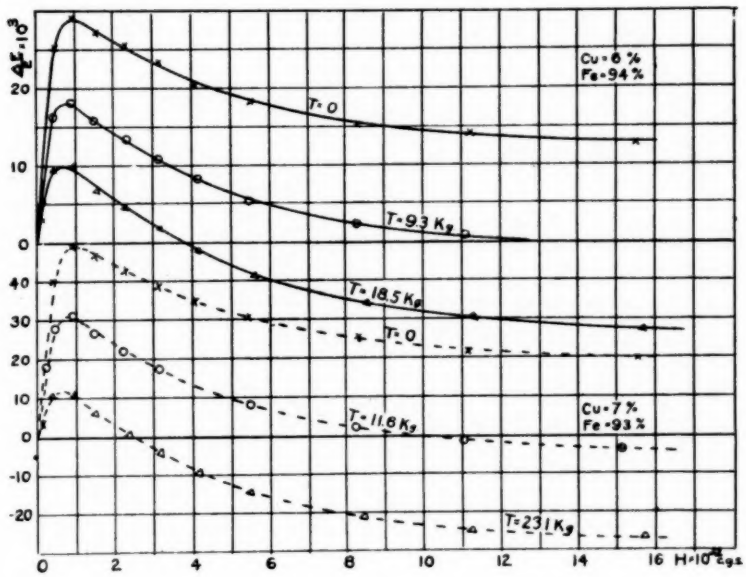
Cu=6 %
Fe=94 %
T=0
T=9.3 Kg
T=18.5 Kg
T=0
T=11.8 Kg
Cu=7 %
Fe=93 %
T=23.1 Kg
H=10 c.g.s

Fig. 6.

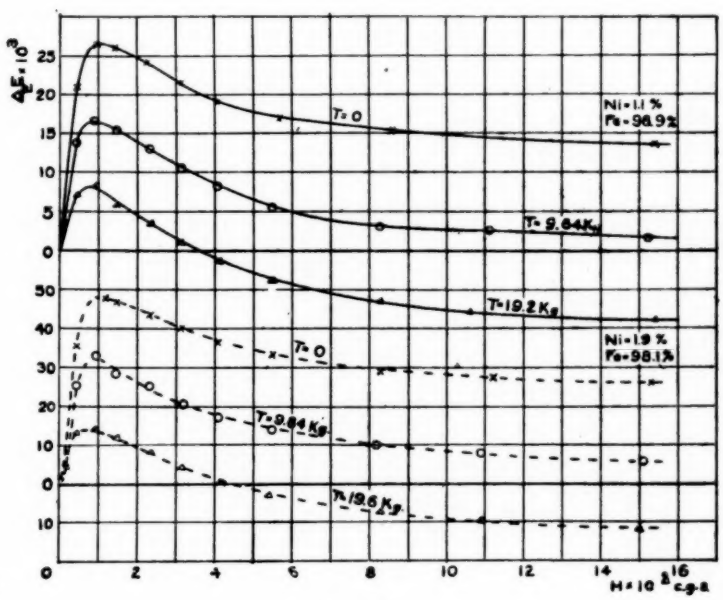
Ni=1.1 %
Fe=98.9 %
T=0
T=9.84 Kg
T=19.2 Kg
Ni=1.9 %
Fe=98.1 %
T=0
T=9.84 Kg
T=19.6 Kg
H=10 c.g.s

Fig. 7.

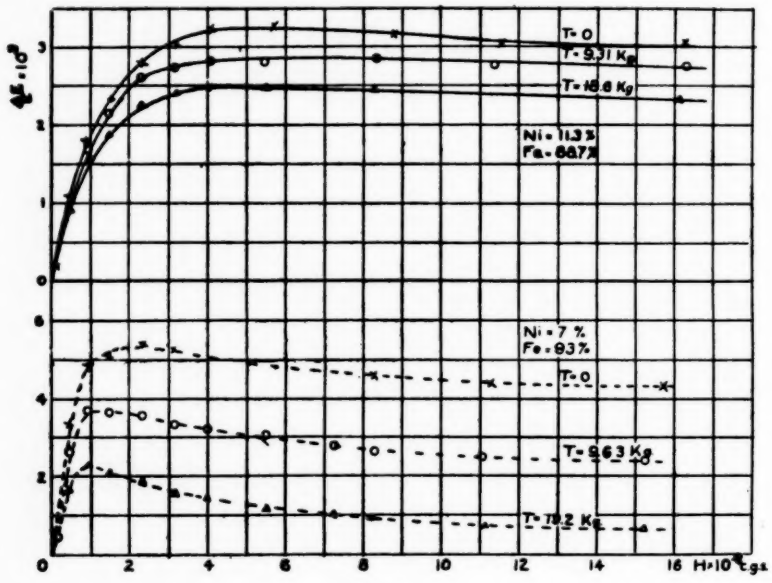

Fig. 8.

The addition of nickel to iron in small quantities causes an increase in the magnitude of the effect over that observed in pure iron. The direction of the thermoelectromotive force and the direction of its change in a magnetic field remain the same as in pure iron until the alloy contains about 7 per cent. nickel where a reversal of direction takes place in both. The alloy then begins to behave more like pure nickel. It still retains some of the characteristics of iron, passing through a maximum and showing a tendency to reverse its direction for sufficiently large tensions. An alloy containing 11.3 per cent. nickel and 88.7 per cent. iron shows more clearly the characteristics of nickel. The effect passes through a maximum as in the other sets of curves but the decrease after the maximum is passed is very gradual. The application of tension causes a decrease in the magnitude of the effect for all values of the magnetic field while in nickel it caused a decrease for low fields and an increase for large fields. The reversal of direction obtained in the preceding cases can not be realized in these alloys.

The longitudinal change of resistance in two of these copper-iron alloys has been represented in Fig. 9 and the observations on the nickel-iron alloys in Fig. 10. In each case the application of tension decreases the change of resistance. The change of resistance when the specimen is completely magnetized is somewhat smaller in those alloys which contain the greater percentage of copper. On the other hand the initial value of this change of resistance in pure iron for low magnetic fields is somewhat

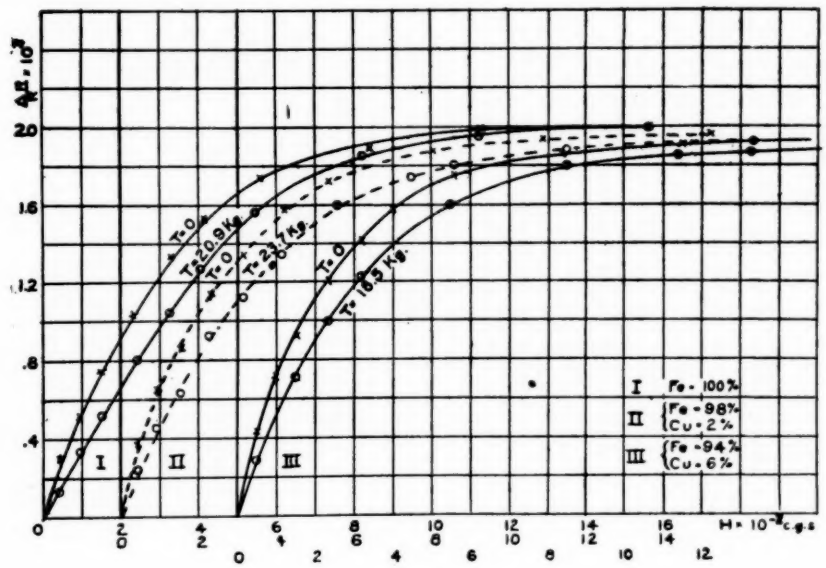
T=0
T=20.9 Kg.
T=0
T=23.7 Kg.
T=0
T=18.5 Kg.
I Fe - 100%
II Fe - 98% Cu - 2%
III Fe - 94% Cu - 6%
H = 10⁻² c.g.s

Fig. 9.

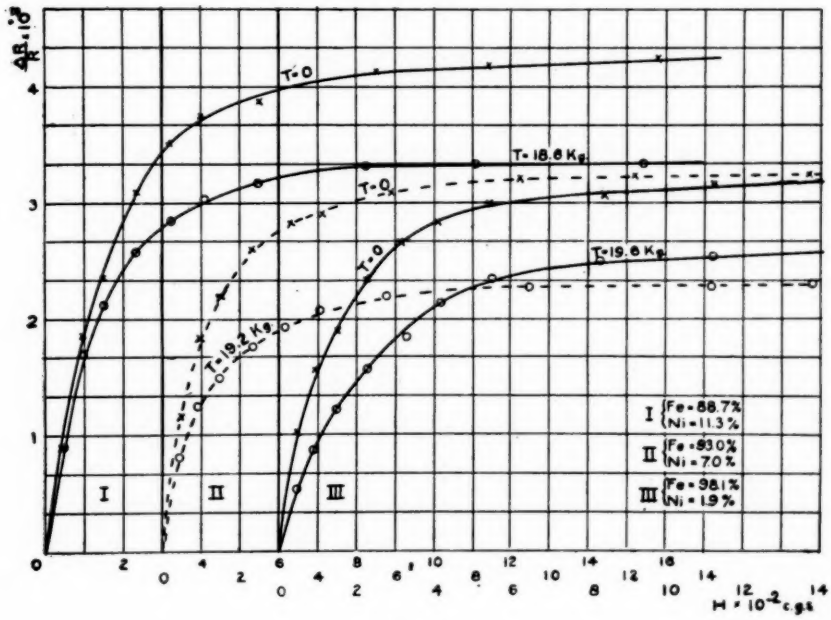
T=0
T=18.6 Kg.
T=0
T=19.8 Kg.
T=0
T=19.2 Kg.
I Fe = 88.7% Ni = 11.3%
II Fe = 93.0% Ni = 7.0%
III Fe = 98.1% Ni = 1.9%
H = 10⁻² c.g.s

Fig. 10.

less than it is in the alloys containing copper. From Fig. 10 it is seen that the addition of nickel to iron increases the change of resistance produced by the magnetic field. It is also seen that the effect of tension is greatest where the amount of nickel is largest.

The upper curve of Fig. 11 shows the Hall constant as a function of the

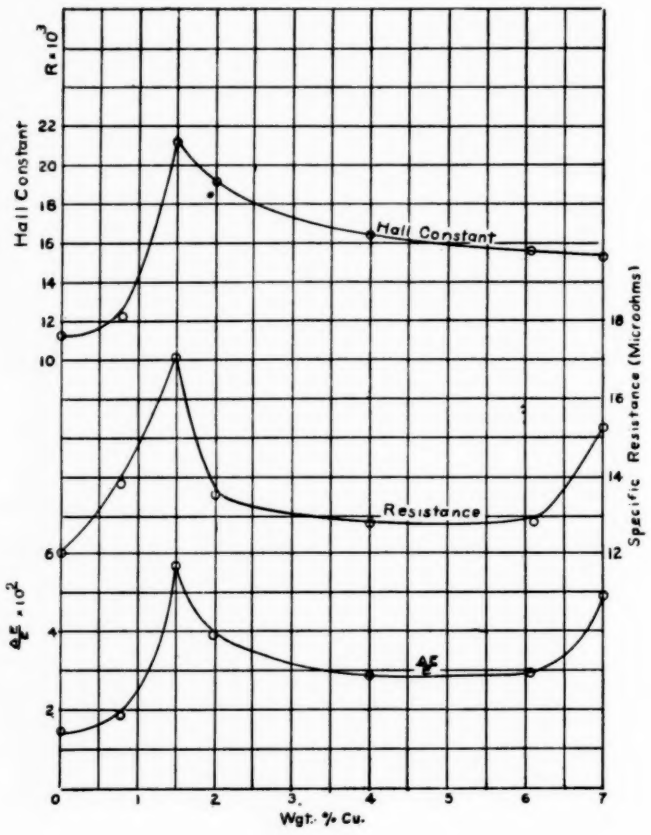

Fig. 11.

concentration of copper. This curve is taken from a former paper by the author.[1] The middle curve represents the specific resistance of these alloys. These resistances were determined by Burgess and Aston.[2] In the lower curve the fractional change in the thermoelectromotive force has been plotted against the concentration of the copper in the alloys. These changes in thermoelectromotive forces are those produced by a magnetic field of 98 gauss when the wire was not under tension. The similarity between these curves is quite evident. They have essentially

[1] Smith, PHYS. REV. (2), 17, 23, 1921.

[2] Burgess and Aston, Met. and Chem. Eng., 8, 79, 1910.

the same characteristics. There is a cusp in each curve where the alloy contains 1.5 per cent. copper. This interrelation for which there seems to be no satisfactory explanation indicates a dependence of all of these effects on some common property of the metals and alloys.

Discussion of Results.—The sources which may be thought of as operating to produce these changes of length, resistance and thermo-electromotive force are changes in the mean free path of the electron, in the number of electrons, in the amplitude of vibration of the atoms and in their frequency of vibration. The change in the mean free path of the electrons would arise from the molecular rearrangement and also from the change in path produced by the action of the magnetic field on the electrons. From this point of view the molecular rearrangement with its accompanying changes in the electric and magnetic forces would be entirely responsible for the change of length and a parallelism between the change of length and the change of resistance would be expected only when the influence of the molecular rearrangement on the mean free path is large in comparison with the effect of the magnetic field on the mean free path.

The application of tension might be expected to decrease the effect of the magnetic field on molecular rearrangement and so decrease the change of resistance and change of length arising out of molecular rearrangement. Since it has been seen that the observed effect in iron and in the iron-copper alloys may be regarded as made up of two parts and that one of these parts seems to be nearly wiped out by sufficiently large tensions it may be that part of the total effect represented by Curve *A* (Fig. 2) arises out of molecular rearrangement produced by the magnetic field. In view of the fact that this part of the effect is missing in nickel it would then be necessary to conclude from this point of view that molecular rearrangement gives rise to a small part of the effect in nickel.

Assuming that the number of free electrons is not changed by the action of the magnetic field Heaps[1] finds on the basis of the gas-free electron theory a proportionality between the fractional change of resistance and the fractional change of length in a longitudinal magnetic field. He thus arrives at the relation,

$$\frac{\Delta R}{R} = -\frac{\Delta \lambda}{\lambda} = -C\frac{\Delta l}{l},$$

where ΔR is change of resistance,

λ and $\Delta\lambda$ are mean free path and change of mean free path respectively,

l and Δl are length and change of length respectively.

[1] Heaps, PHYS. REV. (2), 6, 34, 1915.

Here it is seen that an increase in resistance is associated with a decrease in mean free path and a corresponding decrease in length.

If one holds to the constancy of the number of free electrons in the magnetic field it is not possible to explain the parallelism between the change of length, change of resistance and change of thermoelectromotive force on the basis of the gas-free electron theory. If, however, the number of free electrons is a function of the magnetic field and not the same function at different temperatures then the application of the magnetic field might set up a thermoelectromotive force between the ends of the wire. On the basis of these experiments showing the change in the thermoelectromotive force in a magnetic field it seems impossible to accept the assumption of Heaps that the number of free electrons is independent of the magnetic field.

It is of interest to consider these observations in connection with the gap theory of electric conduction developed by Bridgman.[1] From the point of view of this theory it is considered that the electrons pass without resistance through the atom and that the vibrations of the atoms determine the chance that an electron may pass from one atom to the next. This chance is a function of the amplitude of atomic vibration and of the distance from atom to atom. The greater the mean distance between atomic centers the greater the difficulty which the electron encounters in jumping the gap. It is, however, assumed that when the atoms are at rest the electrons encounter no resistance in passing across the gap provided the separation of atomic centers is not too great. If the mean distance between the atomic centers alone determines the probability that an electron pass from atom to atom, an elongation produced by the magnetic field would be associated with an increase in resistance, since the greater the distance between the atoms the greater the resistance of the metal. But in the case of nickel and possibly in the case of iron it has been seen that a contraction has been accompanied by an increase in resistance. It would, therefore, be necessary to conclude that the amplitude of vibration of the atoms is the controlling factor in determining these changes. The vibrations of the atoms might easily be considered different in the magnetic field from their vibrations in the absence of the field. Now the magnetic field produces an increase of resistance and Bridgman finds that the resistance is proportional to the square of the amplitude of vibration. Since the resistance is increased by the magnetic field it would follow from this theory that the amplitude of vibration has been increased by the magnetic field. Since with this increase in resistance there has been found to be associated a decrease in length and therefore a decrease in the distance between atomic centers we are

[1] Bridgman, PHYS. REV., N.S., 17, 161, 1921.

forced to conclude that the amplitude of vibration is greatest where the distance between the atoms is least. This does not seem to be a very reasonable conclusion unless the considerations introduced by Bridgman to explain the anomalous behavior of bismuth and antimony under pressure be carried over to the explanation of this difficulty. Accepting the assumptions of Grüneisen, Bridgman concludes that in these cases it may be possible to have an increasing amplitude of vibration with an increasing pressure and therefore an increase in resistance. The same reasoning would account for the fact that a contraction in the magnetic field is associated with an increase of resistance. This method of reasoning on the whole does not seem very satisfactory and it is necessary to conclude that the gap theory of electric conduction does not give a very satisfactory explanation of the fact that a decrease in length accompanies an increase in resistance in the magnetic field. In its present development this theory does not cover thermoelectric effects and has therefore no suggestion with respect to the relation between the change in thermoelectromotive forces and changes of resistance and length.

Another line of attack lies in assuming that the number of free electrons is a function of the frequency of the atom and that this frequency is changed by the application of tension and also by the magnetic field. The magnetic field produces a change in the orientation of the molecules and probably a change in the electric and magnetic forces acting in the interstices between the atoms. An elongation accompanying magnetization would increase the distance between the atoms and consequently decrease the electric and magnetic forces operating in the vacant spaces between the atoms. This decrease in the electric and magnetic forces would also produce a decrease in the frequency of vibration of the atom. If it be assumed, in agreement with March,[1] that an increase in the frequency causes a decrease in the number of free electrons, a contraction caused by the longitudinal magnetic field will be accompanied by an increase of resistance. This result is in agreement with the observations on nickel. This point of view would also offer a possible explanation of the change in thermoelectromotive force. When there is a change in the number of free electrons due to an elongation or a contraction of the metal in a magnetic field there would be a change in the concentration of the electrons. Since the wire is unequally heated this change in concentration might not be the same at the hot and the cold junctions. Hence thermoelectromotive forces would be set up. Their direction would depend on whether the magnetic field produced greater or less changes in the concentration as the temperature is increased.

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[1] March, Ann. d. Phys. 49, 710, 1916.

THE LUMINESCENCE OF INCANDESCENT SOLIDS.

BY E. L. NICHOLS AND H. L. HOWES.

SYNOPSIS.

Luminescence of Incandescent Oxides.—Some oxides, when heated to a temperature lying within a definite and sometimes narrow range, emit radiation in a limited region of the spectrum far in excess of the radiation emitted in that region by a black body at the same temperature. The excess is ascribed to luminescence. As a striking example, the blue radiation from niobium oxide at 560° C. is about 85,000 times the corresponding radiation from a black body, the ratio decreasing with increasing temperature until it is 1.35 at 1037° C. just before the oxide melts.

The oxides of beryllium, magnesium, calcium, aluminum, silicon and zirconium also show a blue glow, relatively strongest at the lowest stage of incandescence, decreasing to a minimum, then increasing to one or two crests corresponding to outbursts of blue luminescence between 1100° and 1500° C.

Intensity-temperature curves for the red, green and blue radiations from the oxides of samarium, gadolinium, gallium, niobium, erbium, cerium, praesodymium and neodymium, from 700° to 1550°, show that all except cerium emit a blue or green-blue glow, and all but niobium and neodymium have one or two red, green and blue outbursts above 1000° C. Luminescence is different from temperature radiation not only in its variation with temperature and in its spectrum distribution but also in showing marked fatigue effects and in varying with the previous heat treatment and with the mode of heating used. The effect for any oxide is also sensitive to slight impurities as shown by tests of a *synthetic ruby* and a crystal of *calcium fluoride* containing rare earths.

Luminescence is probably a phenomenon of instability associated with a chemical change such as oxidation or with the physical disturbances which the oxides undergo as they are heated and which are manifested in changes of electrical conductivity, crystal structure and other properties.

Luminescent Emission Bands of Neodymium Oxide occur approximately at *wavelengths* 525, 550, 570, 615 and 660 $\mu\mu$. At 735° C. these bands were brighter than corresponding black-body radiation, but their excess *intensity* decreased, relatively, with increasing temperature until at 1010° they had disappeared into the continuous background of thermal radiation.

THE following substances when heated to incandescence emit light other than that which they would be capable of radiating as a result of their temperature alone; in a word they are luminescent:

1. The oxides of certain elements (grouped below as they occur in the periodic table):

II.	III.	IV.
Beryllium	——	——
Magnesium	Aluminum	Silicon
Calcium	——	Titanium[1]
Zinc	Gallium	Zirconium

[1] The detailed discussion of the luminescence of titanium oxide is reserved for a later paper.

These are all refractory oxides, white or nearly white in color, *i.e.*, transparent when in mass, as are nearly all known luminescent solids.

Not all refractory, white oxides are luminescent by incandescence however, germanium oxide and thorium oxide, of those tested, having failed to show the effect.

On the other hand it is as yet by no means certain that some oxides of lower melting point such as barium oxide, strontium oxide, etc., do not luminesce at the stages of incandescence of which they are capable. They are not amenable to the methods employed in this paper and the exploration by other means has not been undertaken excepting in the case of zinc oxide.

2. Certain of the rare earths, *i.e.*, gadolinium oxide; samarium oxide; niobium oxide, with tantalum as an admixture; the oxides of praesodymium and of neodymium; the oxides of cerium and of erbium.
3. Certain mixtures such as:—$Al_2O_3 + 2\% Cr_2O_3$ (as in synthetic ruby). Calcium Fluoride (a fluorite crystal said to contain the rare earths).

METHOD OF OBSERVATION.

The instrument used in detecting luminescence and in determining its brightness was an optical pyrometer, based upon the Morse gauge, in which a tungsten filament in the focal plane of a telescope of short focus, low power but rather large aperture is superimposed upon the image of the surface the brightness of which is to be determined.

With this pyrometer we measured the brightness I_0 of the incandescent oxide under observation and compared the same with the brightness I_{bb} of a black body at the same temperature. Both I_0 and I_{bb} were expressed in terms of the brightness of the black body at 1000° C. which was taken as a convenient arbitrary unit. The emission of the luminescent oxide, as contrasted with that of the black body under like conditions was given by the ratio, I_0/I_{bb}.

For the most direct and positive determination of this ratio observations were made upon the two incandescent surfaces mounted side by side and subjected to precisely the same process of heating. The most satisfactory arrangement was found to be that indicated in Fig. 1 *B*, where the black ring represents a surface of uranium oxide and the inner disk a coating of the oxide to be studied. The image of the filament of the pyrometer lamp is seen against this pattern.

At the red heat, say 700° C., since these white oxides are exceedingly poor radiators, temperature radiation alone would give us the condition

shown in Fig. 1 *A*, where the disk of white oxide is dark compared with the surrounding ring of black oxide and where the filament may be brought to a degree of incandescence such as to be dark against the black body as a background and bright against the central disk. Luminescence of sufficient intensity will reverse this effect as in Fig. 1 *B*.

Fig. 1.
The pyrometer field.

When, as is frequently the case, the luminescence is confined to one end of the spectrum, both appearances may be observed in the same specimen by shifting the color screen in the eyepiece from red to blue. This is true at the lower stages of incandescence for the oxides of beryllium, magnesium, calcium, aluminum, silicon and zirconium.

For these substances it was therefore possible to determine:

1. The actual black-body temperature and the corresponding brightness I_{bb} by settings on the uranium oxide made through a red screen of equivalent wave length .65 μ.
2. The black-body temperature pertaining to the temperature-radiation from the white oxide: this by settings on the white oxide through the red screen.
3. The brightness of luminescence plus temperature radiation by observing through a screen transparent to the wave-lengths of the luminescent glow.

As will be seen later the luminescence was so great as compared with the temperature-radiation up to nearly 1000° C. that the latter could be ignored.

Mode of Heating.

The surfaces under observation were heated by a hydrogen flame impinging upon them vertically and normally from above, the axis of the flame being concentric with the disk of oxide. The flame, which was from a blast lamp of the usual form, was supplied with sufficient oxygen to give it stability and direction. It might be described as an oxy-hydrogen flame with minimum oxygen.

The choice of this means of producing incandescence was not based primarily upon the rapidity with which temperatures up to 1600° C. can be attained, the ease with which they can be maintained nor the facility with which one can pass from one temperature to another.

The main consideration was that the effect we were seeking is only indirectly related to temperature but is greatly stimulated and enhanced by the conditions existing in the oxy-hydrogen flame.

LUMINESCENCE VERSUS TEMPERATURE-RADIATION.

For the purposes of this paper all radiation in excess of the black-body radiation pertaining to the temperature in question is to be classed as *luminescence*. Radiation due to temperature alone, *i.e.*, following the recognized laws relating radiation to temperature, will be designated simply as *temperature-radiation*. In other words it will be assumed, in accordance with accustomed usage, that a selective radiator emitting light by virtue of its temperature alone may have regions of its spectrum approaching the intensity of the corresponding regions in the spectrum of a black body at the same temperature but that its brightest bands cannot anywhere pass beyond the envelope which surrounds the energy area for the radiation of the black body in question.

It will suffice then to show that the radiation from the various substances already named surpasses that from a black body, in certain parts of the spectrum and throughout certain definite ranges of temperature, in order to establish the fact that we have to do with some form of luminescence.[1] To that end the simple method of observation already briefly outlined is obviously well adapted.

Luminescence of this sort, which is superimposed upon the temperature-radiation of the substance, appears and after increasing to a maximum disappears within a definite and often a comparatively narrow

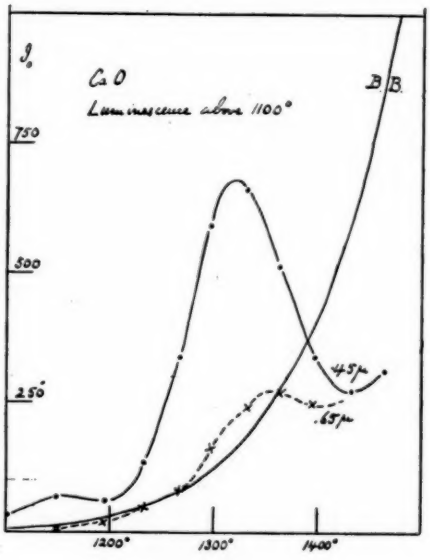

Fig. 2.

Luminescence superimposed on black-body radiation.

[1] Various other characteristics suggestive of the better known types of luminescence will appear in the course of this presentation.

range of temperature. Fig. 2 illustrates such an outburst of luminescence from calcium oxide at about 1300° C.

In this diagram the curve B.B. represents the normal increase in brightness of a black body between 1100° and 1500°. The other curves indicate the brightness of the glowing oxide in the red (.65 μ) and in the blue (.45 μ). It may be noted that *in passing from 1300° to 1400° the calcium oxide, instead of increasing in brightness according to the law of temperature radiation, actually falls off* about fifty per cent.

It had been our purpose in these measurements to separate luminescence as fully as possible from temperature radiation by selecting mutually exclusive screens and this separation is very thoroughly accomplished in the case of the six oxides just mentioned, at least for temperatures below 1000°. In this outburst depicted in Fig. 2 it will be seen that even the red end of the spectrum is somewhat enhanced.

THE BLUE GLOW.

At the lowest temperatures at which visible radiation from these oxides can be detected the ratio I_0/I_{bb} reaches extraordinary values. The blue of the spectrum (luminescence) is many times, often many hundreds

TABLE I.

Luminescence of Beryllium Oxide and Magnesium Oxide.

Temp. C.	BeO.				MgO.			
	I_0.		I_0/I_{bb}.		I_0.		I_0/I_{bb}.	
	Red.	Blue.	Red.	Blue.	Red.	Blue.	Red.	Blue.
665°	.00000025	.0563	.000195	473	.00000018	.0202	.00140	156.7
735°	.0000016	.0795	.000867	65.8	.000026	.0320	.00214	45.0
837°	.00067	.295	.0271	12.0	.00033	.423	.0135	17.2
960°	.038	1.44	.0832	3.14	.0202	3.63	.0482	8.77
1037°	.210	1.95	.109	1.00	.165	8.91	.0847	4.57
1097°	1.00	3.31	.169	.561	1.077	16.1	.182	2.72
1145°	2.46	6.73	.186	.511	....	....	....	....
1190°	6.75	13.0	.252	.423	9.77	26.4	.367	1.04
1228°	72.5	110	1.580	2.44	....	....	....	....
1263°	146	180	1.91	2.35	26.6	36.7	.347	.479
1294°	229	230	1.87	1.99	....	....	....	....
1328°	295	254	1.66	1.43	55.6	72.0	.312	.404
1394°	513	.316	1.32	.813	122.9	139	.257	.356
1429°	....	....	....	....	182	194	.313	.333
1462°	767	513	.927	.620	285	277	.344	.334
1488°	910	600	.830	.535	...	...	....	....
1527°	1,181	773	.728	.477	745	525	.460	.324
1580°	1,641	1,052	.610	.391	1,614	1,012	.600	.375
1606°	1,928	1,282	.564	.375	2,309	1,387	.675	.406

of times, brighter than the corresponding regions of the spectrum of the black body at the temperature in question while the temperature-radiation from the oxide, as indicated by the intensity of the red end of the spectrum, is only a few thousandths of that from the black body. That this is a general statement for these oxides may be seen from the following tables (see values for 665° and 735°).

In Tables I., II. and III. are given the brightness I_0 of six of the oxides under consideration at wave lengths .45 μ and .65 μ, at various temperatures up to about 1600°; also the ratio I_0/I_{bb} throughout this range.

TABLE II.

Luminescence of Calcium Oxide and Aluminum Oxide.

Temp. C.	CaO.				Al_2O_3.			
	I_o.		I_o/I_{bb}.		I_o.		I_o/I_{bb}.	
	Red.	Blue.	Red.	Blue.	Red.	Blue.	Red.	Blue.
665°	.0000006	.0278	.00432	216	....	....	....	400
735°	.000016	.0646	.01285	52.2	.000026	.083	.0213	67.3
837°	.00292	.336	.114	13.7	.000795	.191	.0324	7.80
960°	.1000	1.46	.240	3.49	.173	1.54	.377	3.36
1037°	.802	7.31	.411	3.75	1.25	6.95	.639	3.56
1097°	2.69	25.0	.454	4.19	2.63	21.4	.444	3.61
1145°	6.92	41.7	.522	3.11	2.70	22.4	.209	1.73
1190°	17.5	58.2	.656	2.18	4.31	24.4	.162	.916
1228°	33.1	87.6	.725	1.91	9.55	26.9	.209	.590
1263°	40.7	151	.531	1.97	19.7	59.0	.257	.767
1294°	61.7	254	.535	2.20	33.4	76.7	.290	.665
1328°	120	351	.671	1.97	76.5	164	.431	.923
1362°	264	310	.994	1.17	141	141	.531	.531
1394°	345	226	.887	0.582	1,432	530	3.63	1.36
1429°	422	190	.725	.326	....	....	....	....
1462°	507	226	.613	.274	2,240	1,102	2.70	1.33
1488°	624	261	.570	.233	....	....	....	....
1527°	871	327	.536	.202	1,799	1,799	1.11	1.11
1580°	1,225	578	.455	.215	....	....	....	....
1606°	1,429	795	.381	.232	....	....	....	....

These are the substances whose luminescence at the lowest stages of incandescence has been termed the *blue glow*.[1] They are among the poorest temperature-radiators known and when heated are visible chiefly because of their luminescence.

The region designated as "blue" in the columns of Tables I., II. and III. is really a band, the precise limits of which are somewhat difficult to

[1] Nichols and Howes, Journal, Optical Society of America, VI., No. 1, 1922.

TABLE III.

Luminescence of Silicon Dioxide and Zirconium Dioxide.

Temp. C.	SiO_2.				ZrO_2.			
	I_o.		I_o/I_{bb}.		I_o.		I_o/I_{bb}.	
	Red.	Blue.	Red.	Blue.	Red.	Blue.	Red.	Blue.
655°	.00000076	.0382	.00059	195	.0000026	.00684	.0204	53.1
735°	.0000026	.0708	.0021	57.3	.000077	.0382	.0621	30.9
837°	.00059	.341	.0239	13.9	.0039	.403	.161	16.4
960°	.0275	1.65	.0600	3.59	.1210	3.41	.288	8.15
1037°	.191	4.42	.0977	2.26	1.20	6.91	.617	3.50
1097°	1.10	11.0	.186	1.86	6.34	19.2	1.07	3.25
1190°	8.51	35.3	.316	1.33	24.5	87.5	.923	3.29
1263°	41.2	89.1	.537	1.16	59.0	146	.770	1.91
1294°	100	167	.865	1.44	...	...	...	....
1328°	233	316	1.31	1.77	155	233	.870	1.31
1362°	...	...	....	....	254	317	.979	1.19
1394°	614	631	1.58	3.09	419	397	1.07	1.00
1429°	...	...	....	....	769	610	1.32	1.04
1462°	1,390	1,902	1.68	2.30	1,150	798	1.38	.990
1527°	2,500	2,566	1.54	1.55	1,950	1,102	1.20	.679
1580°	...	...	....	....	2,620	1,500	.973	.427

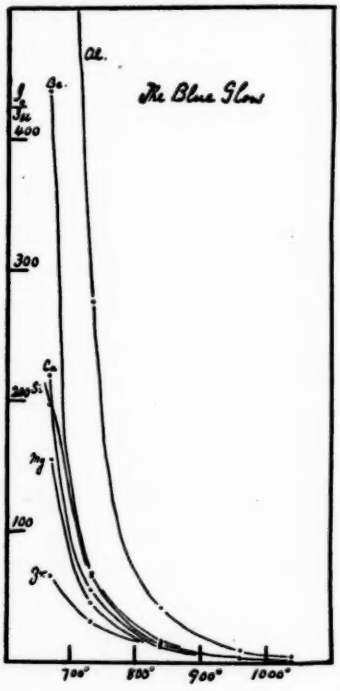

Fig. 3.

The blue glow of six oxides.

determine since it is superimposed upon the spectrum of the temperature-radiation.

It may, however, be discerned under favorable conditions and may be described as lying approximately between .4 μ and .5 μ, but varying as between the various oxides. Estimations for MgO were .48 μ to .42 μ with a maximum at .45 μ, and .45 μ has been taken as the equivalent wave-length.

Fig. 3 shows how the values of I_0/I_{bb} fall off with rising temperatures from the highest readings, which were invariably at the lowest temperature at which it was possible to measure, to values of the order of unity. The curves are approximately exponential. A diagram to this scale indicates nothing of the important outbursts above 1000° where the ratio is small but the actual intensities large, nor does it show the tempera-

ture-radiation of the oxides which for this lower stage of incandescence is too small to appear above the base line.

For temperatures above 1000° we may increase the scale of ordinates

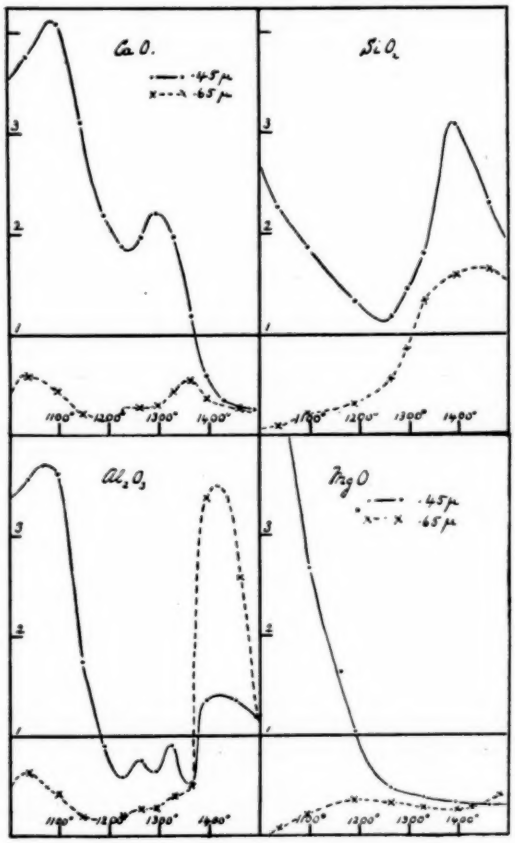

Fig. 4.

Luminescence of CaO, SiO_2, Al_2O_3 and MgO above 1000° C.

as in Figs. 4 to 8 which (except in the case of MgO) display outbursts of luminescence at these higher temperatures.

TABLE IV.

Outbursts of Luminescence above 1000° in the Oxides given in Tables I., II. and III.

Substance.	Temperatures of Crests.
CaO	1100° and 1300°
Al_2O_3	1075° " 1425°
ZrO_2	1150° " 1450°
SiO_2	1400°
BeO	1225° ....

A discussion of the possible significance of these outbursts will be given in a later paragraph.

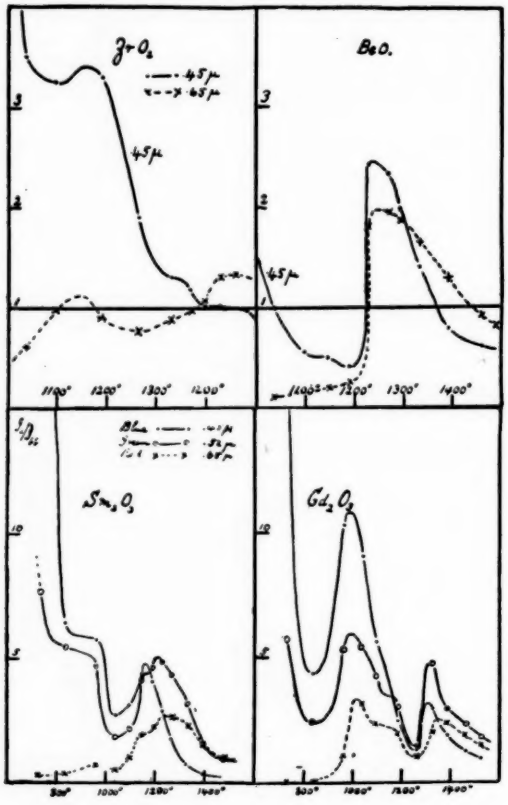

Fig. 5.

Luminescence of ZrO_2, BeO, Sm_2O_3 and Gd_2O_3.

LUMINESCENCE OF THE INCANDESCENT RARE EARTHS AND OF THE OXIDES ERBIUM AND CERIUM.

Samarium and gadolinium oxides (Table V. and Fig. 5) have two features in common, as regards their luminescence, with those oxides in which the blue glow occurs.

1. Radiation in the red rises from small relative intensities at the lowest temperatures.

2. The value of I_0/I_{bb} is greatest at the beginnings of incandescence throughout the blue end of the spectrum.

They differ however in that the initial brightness in the green is appreciable at the lowest temperatures and becomes a dominant factor

in the outbursts of luminescence which follow upon the blue glow as the temperature rises.

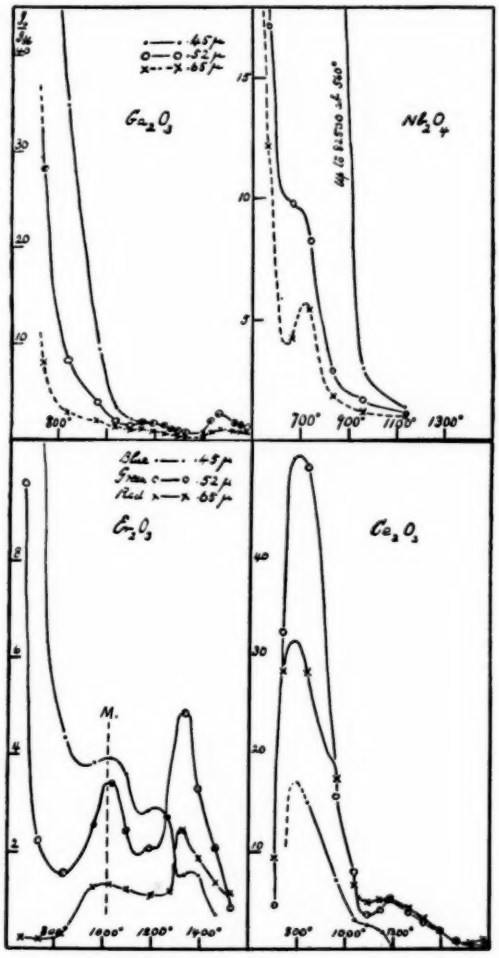

Fig. 6.

Luminescence of Ga_2O_3, Nb_2O_4, Er_2O_3 and Ce_2O_3.

The oxides of gallium and niobium (Table VI. and Fig. 6) represent a further departure in that the largest values of I_0/I_{bb} for the red as well for the green and blue are at the lowest temperatures.

Shortly above 1000° where the niobium oxide was approaching non-selective radiation of an intensity approximately that of a black body, fusion occurred and measurements by our method ended.

This oxide which according to the chemists contained, as is usual, a slight admixture of tantalum oxide, showed by far the brightest lumines-

TABLE V.

Luminescence of Samarium Oxide and of Gadolinium Oxide.

Substance.	Temp. C.	I_o.			I_o/I_{bb}.		
		Red.	Green.	Blue.	Red.	Green.	Blue.
SaO.....	735°	.00049	.0094	.680	.396	7.64	55.1
	837°	.0102	.107	1.55	.425	5.47	6.40
	960°	.314	1.94	2.40	.750	4.64	5.73
	1037°	1.10	3.56	5.31	.563	1.83	2.72
	1097°	6.31	12.9	18.5	1.06	2.18	3.13
	1145°	25.9	55.0	56.0	1.96	4.15	4.23
	1190°	58.9	122	138	2.21	4.60	4.07
	1228°	123	221	132	2.69	4.83	2.88
	1263°	202	331	135	2.63	4.31	1.76
	1328°	417	502	135	2.34	3.16	.750
	1394°	576	611	145	1.48	1.57	.371
	1462°	828	716	271	1.00	.927	.206
GdO.....	735°	.000051	.000708	.0200	.0417	.573	16.2
	837°	.000851	.00596	.108	.0347	.243	4.39
	960°	.447	2.30	5.14	1.067	5.16	12.3
	1037°	5.27	10.6	17.6	3.16	5.43	9.02
	1097°	13.9	25.0	33.4	2.35	4.21	5.64
	1190°	51.2	80.2	66.1	1.93	3.02	2.48
	1263°	78.5	112	97.7	1.02	1.45	1.27
	1328°	230	552	340	1.99	4.79	2.94
	1394°	902	1130	726	2.32	2.91	1.86
	1462°	1556	1902	1092	1.88	2.30	1.32
	1527°	2410	2820	1524	1.48	1.74	0.94

cence below 600° of any of the incandescent oxides included in this series of observations. This permittcd readings at 560° at which temperature the intensity through the blue screen was 85200 times that of the same wave lengths from a black body.

In erbium oxide (Table VII. and Fig. 6) we have again the modified blue glow followed at higher stages of incandescence by further outbursts of luminescence.

This substance has been a subject of study since the times of Bunsen on account of the narrow emission bands in its spectrum but it remained for the late W. G. Mallory[1] to show that these bands exceeded the corresponding black-body radiation in intensity.

Mallory explored the visible spectrum through a narrow range of temperature and found a maximum of relative brightness for the red, green and blue regions at about 1000°. The outburst of luminescence at that temperature designated by the vertical line *M*, in Fig. 6 repre-

[1] Mallory, PHYSICAL REVIEW (2), XIV., p. 54.

sents Mallory's effect both as to the approximate temperature and the relative intensity of the red, green and blue regions. His intensities in terms of those of the black body are somewhat larger than ours, which may indicate a more active condition of his luminescent material. It is more likely, however, that working as he did with a spectrophotometer instead of using colored screens, he obtained better defined and more pronounced crests both as to temperature and wave length.

TABLE VI.

Luminescence of Gallium Oxide and Niobium Oxide.

Substance.	Temp. C.	I_o.			I_o/I_{bb}.		
		Red.	Green.	Blue.	Red.	Green.	Blue.
GaO.....	735°	.0100	.0347	.100	8.08	28.1	80.2
	837°	.0733	.209	.851	2.99	8.51	34.7
	960°	.841	1.59	3.94	2.01	3.79	9.40
	1037°	2.60	4.07	6.53	1.32	2.05	3.31
	1097°	6.53	8.51	10.2	1.10	1.43	1.73
	1145°	13.2	22.0	16.8	.995	1.67	1.27
	1190°	26.6	41.7	36.3	1.00	1.57	1.36
	1228°	44.7	63.4	62.4	.978	1.38	1.36
	1263°	53.7	86.1	77.6	.700	1.12	1.01
	1294°	59.6	189	89.1	.515	1.03	.771
	1328°	69.2	155	105	.388	.870	.594
	1394°	143	339	359	.367	.871	.923
	1429°	569	1,097	575	.978	1.87	.988
	1462°	871	2,370	1,097	1.05	2.86	1.325
	1527°	1,679	2,849	2,600	1.03	1.76	1.63
	1555°	2,068	3,350	3,429	.980	1.59	1.62
	1580°	2,341	3,590	4,030	.870	1.33	1.50
NbO.....	560°	.000025	.000035	.174	12.2	17.2	85,200
	665°	.00055	.00126	.277	4.25	9.77	2,150
	735°	.00695	.0100	.398	5.41	8.20	.322
	837°	.0449	.0708	.638	1.83	2.89	26.0
	960°	.513	.692	1.34	1.22	1.65	3.21
	1037°	1.95	2.29	2.66	1.00	1.17	1.35

Mention of this confirmation has already been made in the form of a brief note in *Science*.[1]

Cerium oxide, the luminescence of which is also depicted in Fig. 6, is characterized by the complete absence of blue glow. There is a well-marked outburst at 800° in which the green is dominant and the red about twice as bright as the blue. In a second outburst at 1200° the blue takes no part.

[1] Nichols and Howes, Science, Jan. 13, 1922; p. 53.

THE OXIDES OF PRAESODYMIUM AND NEODYMIUM.

Through the kindness of Professor James, of New Hampshire College, to whom we owe our samples of the rare earths, we were in possession of a sufficient quantity of these substances, which are rarely to be had in a state of satisfactory separation, to permit of the following observations.

We found the two oxides to differ greatly in their radiating properties.

TABLE VII.

Luminescence of Erbium Oxide and Cerium Oxide.

Substance.	Temp. C.	I_o.			I_o/I_{bb}.		
		Red.	Green.	Blue.	Red.	Green.	Blue.
ErO.....	665°	.000032	.00136	.00945	.250	10.6	68.4
	735°	.00026	.00278	.0172	.214	2.25	13.9
	837°	.00679	.0389	....	.277	1.58	4.37
	960°	.543	1.07	....	1.29	2.55	3.83
	1037°	2.52	6.61	7.00	1.31	3.39	3.89
	1097°	6.55	14.5	21.4	1.22	2.45	3.61
	1190°	29.9	58.0	76.7	1.12	2.07	2.88
	1263°	130.4	310	207	1.17	2.74	2.69
	1328°	440	871	275	2.47	4.89	1.54
	1394°	725	1,298	745	1.86	3.33	1.55
	1462°	1,148	1,730	575	1.38	2.09	.695
	1527°	1,820	1,413	917	1.12	.870	.565
CeO.....	702°	.0040	.0017	....	8.95	4.72	....
	735°	.0349	.0403	....	28.3	32.6	....
	837°	.692	1.21	.370	28.2	49.5	15.2
	960°	4.92	6.53	3.02	17.7	15.6	7.21
	1037°	13.9	15.3	6.03	7.12	7.85	3.09
	1097°	28.3	21.4	15.1	4.78	3.63	2.55
	1145°	69.5	53.2	25.4	5.25	4.02	1.91
	1190°	133	133	11.7	5.02	5.02	0.44
	1263°	334	304	11.1	4.34	3.95	0.144
	1328°	596	519	25.4	3.34	2.91	.142
	1394°	653	695	87.9	1.58	1.69	.227
	1462°	783	887	113	.950	1.07	.136
	1527°	1,319	1,309	423	.813	.684	.260
	1580°	3,304	1,514	656	1.23	.563	.244

Neodymium oxide at the lower stages of incandescence has several rather narrow well-defined emission bands. These were mentioned by Hartley[1] in 1901 but according to Kayser[2] no study has been made of them.

[1] Hartley and Ramage, Trans. Royal Soc. of Dublin (2), VII., p. 339.

[2] Kayser, Handbuch der Spectroscopie, Bd. VI., Chapter on Neodymium.

A hurried exploration with a hand spectroscope gave as the approximate location of five of these:

.660 μ; .615 μ; .570 μ; .550 μ; .525 μ.

At 735° C. the red and green bands were brighter than the corresponding wave lengths in the spectrum of a black body. At 960° the bands were still visible but relatively weak. At 1010° no bands were seen and the radiation was that of a black body both in intensity and distribution. (See Table VIII.)

TABLE VIII.

Luminescence of the Oxides of Praesodymium and Neodymium.

Substance.	Temp. C.	I_o.			I_o/I_{bb}.		
		Red.	Green.	Blue.	Red.	Green.	Blue.
Pr_2O_3.....	665°	.000051	.....	....	.394	....	....
	735°	.00123	.0308	.0254	1.00	2.49	2.00
	837°	.0308	.0468	.0468	1.25	1.91	1.91
	960°	.537	1.76	2.40	1.28	4.20	5.73
	1037°	3.03	7.08	6.22	1.55	3.63	3.19
	1097°	11.5	17.1	8.04	1.94	2.88	1.35
	1145°	26.6	31.6	11.5	2.01	2.39	.870
	1190°	50.4	53.0	43.9	1.90	1.99	1.65
	1228°	85.1	87.7	52.7	1.86	1.92	1.15
	1263°	123	132	51.2	1.61	1.72	.667
	1294°	157	175	52.7	1.35	1.51	.456
	1328°	181	221	71.1	1.00	1.24	.399
	1394°	302	361	126	.744	.929	.324
	1462°	525	659	146	.643	.796	.176
	1527°	877	1,047	367	.541	.646	.135
Nd_2O_3.....	735°	.00243	.00881	....	1.94	7.00	....
	967°	.0871	.204	.348	.152	.417	.712
	1010°	1.12	1.12	1.42	1.00	1.00	1.26

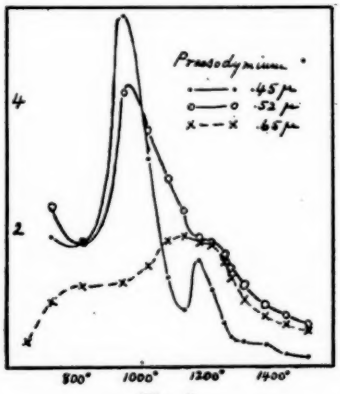

Fig. 7.

Relation of luminescence of ruby and fluorite to that of Al_2O_3 and CaO.

Praesodymium oxide, Pr_2O_3, has a tendency to change into Pr_4O_7 in the oxy-hydrogen flame and our observations probably refer to the latter, which is a nearly black powder, or to a mixture of the two oxides.

No narrow bands were visible at any temperature but the continuous spectrum is by no means devoid of luminescence as may be seen from Table VIII. and Fig. 7. There are clearly at least two separate bands, one involving the g rcea nd blue and having a moderate

maximum at about 960°, the other in the red with a maximum at about 1150°. The blue glow is absent and above 1300° the blue end of the spectrum is relatively so feeble as to give the incandescent oxide a ruddy hue suggestive of lower temperatures.

SECONDARY FEATURES INDICATIVE OF LUMINESCENCE.

1. *Fatigue.*—The first heating of these oxides to moderate incandescence was frequently found to produce a brightness greatly in excess of that existing after a given temperature had been maintained for some time. The decay, as was to be expected, was very rapid at first and had a diminishing rate. No attempt has been made as yet to determine the curve of decay. A few estimates of the initial brightness of magnesium oxide at a temperature of 1220° gave the following result. Observations were for .45 μ.

$$I_0 = 2690; \qquad I_{bb} = 41.3; \qquad I_0/I_{bb} = 65.3.$$

The usual value at this temperature after ignition for several minutes was less than unity (see Fig. 4). The above readings were made about 0.3 second after ignition and are doubtless too late for the actual maximum.

This fatigue has long been known in the case of lime cylinders against which an oxy-hydrogen flame impinges and decay curves were made many years ago.[1]

Probably the limiting value for initial brightness is obtained when we burn a metal like magnesium. W. H. Pickering[2], long before the general laws of radiation had been developed, estimated the temperature corresponding to the spectral distribution of the light from the magnesium flame at 4900° C. It is now easy to check his value which was based upon a purely empirical relation between the ratio of red and blue in the spectrum and the temperature by applying the distribution law to the spectrum of this flame. The result gives about 5000° C. and since the actual temperature of the flame, as studied by F. J. Rogers,[3] cannot be above 2000°, this means that 98% or more of the light must be ascribed to luminescence.[4]

2. *Effects of Heat Treatment.*—As in the preparation of phosphorescent substances for excitation by light or by kathode rays, so here the effects of previous heat treatment are varied and complicated.

In some cases the previous heating of an oxide to full incandescence

[1] Nichols and Crehore, PHYSICAL REVIEW (1), II., p. 161.

[2] W. H. Pickering, Proc. Am. Acad. of Arts and Sciences, 1879–80, p. 236.

[3] F. J. Rogers, Am. J. of Sc., XLIII, p. 301, 1892.

[4] Nichols, Trans. Ill. Eng. Soc., Oct. 10, 1921.

seems to be essential to the blue glow and to other luminescent outbursts belonging to the lower stages (below 1000°). Sometimes, however, heating to moderate temperatures reduces the glow. A sample of beryllium oxide not previously ignited was heated in the H-O flame to about 1000° and after a fairly stable state had been reached was allowed to cool, stepwise, by gradually reducing the flame. In this way the

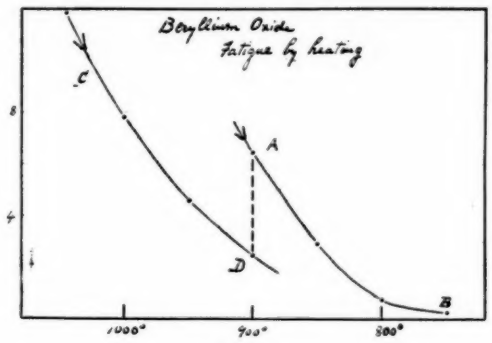

Fig. 8.

Effect of fatigue by heating.

upper curve in Fig. 8 was obtained. The temperature was then increased to about 1300°. The lower curve indicates the brightness on cooling after this treatment.

Heating to incipient fusion, *i.e.*, until the surface of the oxide became mobile as observed with the pyrometer, had in one instance a more striking result.

A sample of aluminum oxide which showed the blue glow and which on further heating step by step developed the usual outbursts at (1000°–1100°) and (1300°–1500°), showed signs of fusion. On cooling stepwise in the flame the outburst at (1300°–1500°) was repeated but of the luminescence at lower temperatures all but a trace was gone. The intensity at 735° as viewed through the blue screen was now $I_0/I_{bb} = 1.02$ instead of the previous value of 67.3.

3. *Influence of the Mode of Heating.*—The type of luminescence now under consideration, unlike the luminescence by flame excitation recently described,[1] is not confined to substances exposed to the action of the hydrogen flame. It is for example possible to see the blue glow when beryllium oxide is heated in a crucible, or when zinc oxide or other oxides are electrically heated on a strip of platinum foil. The effect is however much more intense when the flame is used, and the brightness is greatly affected by changes in the supply of oxygen so slight that the actual

[1] Nichols and Wilber, PHYSICAL REVIEW (2), XVII., p. 453.

temperature, as indicated by the radiation from the black surface, is not appreciably modified.

The following observations upon magnesium oxide using adjustments of hydrogen and oxygen such as to maintain a constant temperature may serve to illustrate this point.

MgO. Temperature 1220° C.; $I_{bb} = 41.3$.

With excess of hydrogen: $I_0 = 57.0$; $I_0/I_{bb} = 1.38$.

With excess of oxygen: $I_0 = 151$; $I_0/I_{bb} = 3.66$.

The general luminescent activity of the oxide was somewhat greater than in the foregoing experiment on fatigue.

It was noted in the course of these trials that the sensitiveness to oxygen seemed to differ with the various oxides and for a given oxide was much greater at some temperatures than at others. This presumably depends on whether the observation is made at a temperature corresponding to one of the outbursts of luminescence.

This is a point not yet definitely established by systematic experiments with several different oxides. It was noted however in the course of our measurements with praesodymium oxide that this substance was exceedingly sensitive to the slightest changes in the supply of oxygen at temperatures around 1000°. Above 1300° where there is little but temperature radiation in evidence this sensitiveness had disappeared.

THE EFFECTS OF ADMIXTURE.

That the photo-luminescence of various sulphides and oxides is due to the presence of certain activating substances and that the kathodo-luminescence of the oxides with which we are concerned is profoundly modified by the minutest traces of the same, has long been known. It was of interest therefore to note the effect of such admixtures upon the luminescence of the incandescent oxides. Two such preparations were at hand with which to make the test.

1. A sample of aluminum oxide heated to 1200° with 2 per cent. of a chromium salt as in the making of synthetic rubies (a finely phosphorescent preparation due to Mr. W. C. Andrews).

2. A crystal of fluorite showing in the kathode tube the narrow line-like bands ascribed to the presence of rare earths. (This was one of the specimens then under spectroscopic observation by Miss Frances G. Wick.)

When incandescent these exhibited the rather complicated series of outbursts shown in Fig. 9. A comparison with the results obtained with Al_2O_3 and CaO respectively show that the luminescence of these oxides forms a component but only a minor part of the display. To render

such a comparison visually easy, the luminescence as seen through a single screen is plotted for Al_2O_3 and the ruby and for CaO and the fluorite in the same diagram.

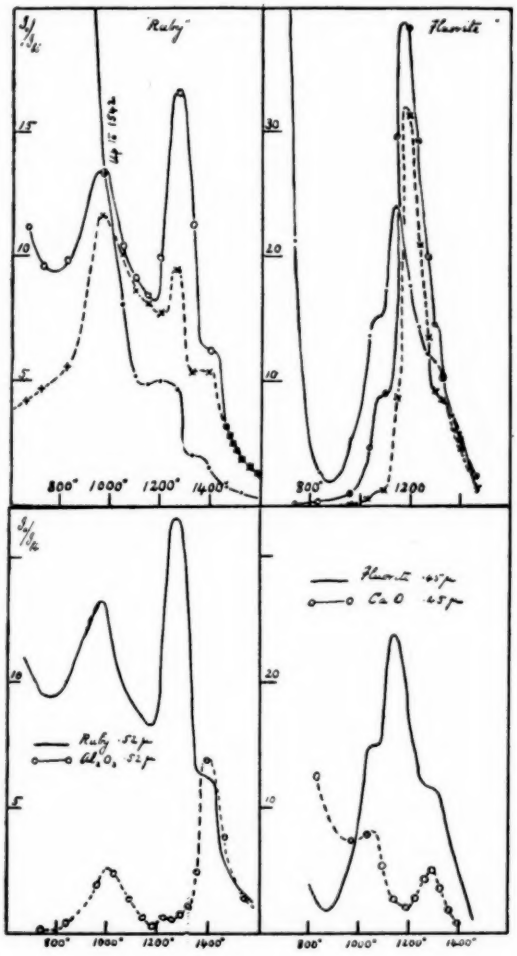

Fig. 9.

Luminescence of praesodymium oxide.

Whether all luminescence within the incandescent range is due to activating admixtures would perhaps be as difficult of positive determination as in the vexed case of kathodo-luminescence. Thus far we have been unable to procure or produce oxides of a purity such that they would not respond to the excitation of kathode-bombardment. Neither have we found any which fail of luminescence when incandescent.

LUMINESCENCE A PHENOMENON OF INSTABILITY.

There is abundant evidence to connect the luminescent glow of these incandescent oxides, between definite temperature limits, with changes in the physical properties of the substance.

That the luminescence of zinc oxide is coincident as to temperature with changes in the electrical resistance and its allied properties has already been pointed out.[1] All the oxides which show the blue glow[2] are known to be going through the change from infinite resistance to low resistance within the range of temperatures through which the glow persists. The outburst manifested by aluminum oxide at (1000°–1100°) occurs where the resistivity curves of Northrup[3] for alundum show an inflection and the more pronounced luminescence of that oxide between 1300° and 1500° coincides with similar irregularities in the relations between temperature and resistivity published by Hering[4] from Northrup's data. Finally the display of luminescence by silica between 1300° and 1500° (see Fig. 4), finds its counterpart in the well-established transformation point of quartz.

It is as though during such rearrangements in the structure, the light-producing process which we term luminescence can go on, a concept which brings the effects here considered into a certain relationship to the views recently urged by Perrin and supported by R. W. Wood. If the light-producing process is an oxidation, following and alternating with partial breakings down, degenerations or reductions under the influence of temperature, the luminescence of incandescent oxides must be regarded as akin to those other types of luminescence for which oxidation is already the established and accepted cause.

PHYSICAL LABORATORY OF CORNELL UNIVERSITY,
November 25, 1921.

[1] Nichols, PHYSICAL REVIEW (2), XVII., p. 430.
[2] Nichols and Howes, Journal of the Optical Society of America, VI., No. 1, 1922.
[3] E. F. Northrup, Metallurgical and Chem. Eng., XII., p. 125, 1914.
[4] C. Hering, Metallurgical and Chem. Eng., XIII., p. 25, 1915.

THE DIELECTRIC CONSTANT OF MICA.

By J. R. Weeks, Jr.

Synopsis.

Dielectric Constant of Mica.—The constant was determined for 18 samples of mica, varying in thickness from 0.005 to 0.073 inch and including 12 different grades. Each sheet was placed between two mercury electrodes and the capacity of the condenser thus formed was determined with a shielded capacity and conductance bridge using alternating current at 1,000 cycles per second. It was found that while thick sheets with plainly visible air films had low dielectric constants, those without such films gave fairly consistent results, running from 6.4 to 9.3 with an average of 8.1. When a thick sheet was split, the thinner sheets had higher constants except in the case of a sample of Canadian amber.

Power Loss in Mica Condensers was too small to determine accurately with the apparatus used, but was higher for stained than for clear micas.

In looking for an average value of the dielectric constant of mica in the handbooks of the Physical Constants of materials such as, the Smithsonian Tables, Kays and Laby, Chemiker Kalender, and Landolt-Börnstein, the writer was impressed with the wide variations found by different investigators. The values given in these reference books varied from 2.5 to 10. It seemed likely that at least a part of this large variation might be due to air pockets or films between the various laminæ, especially since most of these low values were found on rather thick sheets. The high values, on the other hand, might be due to conducting films between the laminæ increasing the effective area of the electrodes. Therefore, it was decided to measure the dielectric constant of different grades of mica, and especially those grades used by other investigators, with a view of making an accurate determination of the dielectric constant and of finding, if possible, the causes of these wide variations.

Accordingly 18 samples of mica of varying thicknesses were obtained, including 12 different grades. Unfortunately it was impossible to obtain all of the grades for which other investigators had given low values. These grades apparently do not reach the New York market (India micas). It was possible, however, to get mica of the same thicknesses as were used in these other investigations. The samples were numbered from 1 to 18. The subscripts A, B and C denote thin sheets split from the original sheet after the first measurement was made.

METHOD.

Most of the sheets did not require cutting, but where necessary the sheet was clamped between brass plates and carefully cut to $3\frac{1}{4} \times 2\frac{1}{2}$ inches with a sharp knife. The sheet of mica was floated upon a copper plate amalgamated with mercury which served as the bottom electrode. This plate was grounded. The top electrode consisted of a hollow brass rectangle $1\frac{7}{8} \times 2\frac{5}{8} \times \frac{1}{4}$ inches high. This rectangle was placed in the center of the sample and filled with mercury.

The capacity of the condenser thus formed was measured with alternating current at 1,000 cycles per second by a shielded [1] capacity and conductance bridge which had been checked against condensers calibrated by the Bureau of Standards. The thickness of the sheet between the electrodes was measured with an accurate micrometer, measuring to 0.0001 inch. Wherever the original sheet was thick enough, it was split into thinner sheets along its natural lines of cleavage and each of these measured as above. Considerable difficulty was experienced in preventing air pockets from forming between the mercury and the sheet on the under side. Every effort was made to reduce to a minimum the errors introduced by these air pockets and in each case the highest obtainable capacity reading was taken as the correct one. The individual capacities varied from 100 to 1,200 mmf. Over this range of capacity the bridge error was less than 1 per cent.

The results of these measurements are given in Table I. There is a probable error not greater than minus 5 per cent. due to air films between the electrodes and the sheet. Check readings given for samples of Madras green 5–*A* and 5–*B* show how closely it was possible to duplicate readings. The sample 5 having a dielectric constant of 2.9, was very badly split and the various laminæ were quite noticeably separated. However, thin sheets split from this sample had dielectric constants of 6.6 to 8.4. It was this effect, namely a thick sheet having a low dielectric constant (due to air films) while thin sheets split from it had a high dielectric constant, which undoubtedly caused the low values given by others. Sample 17 further illustrates the above point. It had a dielectric constant of 4.8 while thin sheets split from it had dielectric constants of 8.4 and 8.6.

While some sheets having plainly visible stains did have a dielectric constant somewhat higher than the average, there was no such pronounced effect as that shown by air films. None of the sheets, however, was badly stained. Sheets 7, 8 and 9 were the only ones having stains

[1] G. A. Campbell, Elect. World and Eng., Vol. XLIII, pp. 647, 1904.

which looked at all like continuous films. These sheets had dielectric constants a little higher than the average value of 8.1.

TABLE I.

Sample.	Thickness Inches.	Dielectric Constant.	Material.
1	.0273	7.9	Madras brown
1-*A*	.0134	7.9	" "
1-*B*	.0143	8.4	" "
2	.0165	8.7	" "
3	.0218	8.7	Madras ruby
4	.0534.	8.1	Canadian amber
4-*A*	.0270	8.0	" "
4-*B*	.0142	7.3	" "
4-*C*	.0071	6.4	" "
5	.0274	2.9	Madras green
5-*A*	.0045	7.0(6.6)	" "
5-*B*	.0048	8.0(7.9)	" "
5-*C*	.0064	8.4	" "
6	.0232	8.0	" "
7	.0122	9.3	Indian brown stained
8	.0052	8.4	" " "
9	.0065	8.9	" " "
10	.0060	8.6	Ruby—source unknown
11	.0031	7.2	Clear—source unknown
12	.0286	8.1	Argentine clear
12-*A*	.0076	8.0	" "
13	.0294	7.4	Brazilian stained
13-*A*	.0104	8.1	" "
13-*B*	.0190	8.2	" "
14	.0158	8.6	Brazilian clear
15	.0643	6.6	Argentine stained
15-*A*	.0113	8.0	" "
15-*B*	.0117	5.9	" "
15-*C*	.0068	7.7	" "
16	.0674	5.6	Indian brown clear
17	.0736	4.8	" " "
17-*A*	.0122	8.6	" " "
17-*B*	.0097	8.4	" " "
18	.0233	8.4	Argentine clear
18-*A*	.0088	8.8	" "

Samples 5, 15-B, 16 and 17 had visible air films.
Samples without visible air films—Average 8.1
Maximum 9.3
Minimum 6.4

The phase angle also was measured, but the bridge readings were too small to make an accurate determination possible. The phase angle readings showed that stained sheets had higher losses than clear sheets.

CONCLUSIONS.

1. When air films in the interior of the sample of mica were eliminated by splitting it along its natural lines of cleavage into thin sheets, in no case was the dielectric constant less than 6.4.

2. Where air films were plainly visible, the dielectric constant was low (2.9 to 4.8).

3. It seems likely that the low values given by some investigators undoubtedly were due to air films between the laminæ. These air films were in most cases very hard to see without carefully examining the edges of the sheets.

4. Stained sheets did not show a dielectric constant enough higher than the average value of 8.1 to determine the effect of stains in mica upon the dielectric constant.

5. No difference in the dielectric constant is readily discernible between the different grades or kinds of mica which were tested.

RESEARCH LABORATORIES OF THE
AMERICAN TELEPHONE AND TELEGRAPH COMPANY
AND WESTERN ELECTRIC COMPANY, INC.

A NEW GYROSCOPIC CONSTRUCTION IN SIMPLE VECTORS.

BY WILL C. BAKER.

SYNOPSIS.

Simple Vector Representation of the Steady Precession of a Gyroscope.—By means of vector angular momentum diagrams, the quadratic for steady precession is derived graphically, and the variation in the steady precession at constant angle with change of applied couple is represented so as to be easily visualized. The couple required to prevent precession due to the earth's rotation is also given in a vector diagram.

IN all cases of the free precession of a rotating body, the looped or oscillatory path of the axis is an essential part of the motion. Yet, whenever the angular momentum of spin is high enough, these oscillations become vanishingly small. As most of the cases of interest to the average student are of this type, *i.e.*, the approximately steady precession, the following geometrical constructions are of interest.

Following the usual plan, resolve the precessional velocity, $\dot{\psi}$, into (1) a compoment $\dot{\psi}\cos\theta$ about OC (Fig. 1, *a* and *b*) and (2) $\dot{\psi}\sin\theta$ about OE. Take C, A, A, as the moments of inertia of the top about the axes OC, OE, OD, and let ω be the angular velocity of spin about OC. Thus the components of angular momentum are $C(\omega + \dot{\psi}\cos\theta)$, or Cn, about OC and $A\dot{\psi}\sin\theta$ about OE. Represent these at a given instant by the vector diagram of Fig. 2 in which $OS = Cn$, and $SQ = A\dot{\psi}\sin\theta$. Thus

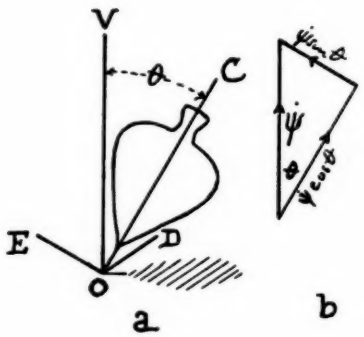

Fig. 1.

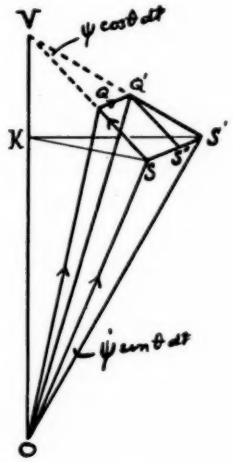

Fig. 2.

OQ is the resultant angular momentum at the instant when OS is parallel to the axis of the top. Now, instead of attacking this plane figure, $OVQS$, algebraically as in the well-known construction of Sir George Greenhill,[1] let us represent on the same diagram (in three dimensions) the position of these vectors after the lapse of a small time dt.[2] The plane defined by OSV will have rotated through the small angle $\dot{\psi}dt$ (given by SKS' on the figure, and as the final angular momentum OQ' is equal to the initial value OQ plus the vector QQ', the latter must be the angular impulse $(Mgh \sin \theta)dt$, received by the system during the interval. Here M is the mass, and h the distance from the pivot to the center of mass of the top. Thus we have:

$$\begin{aligned} QQ' &= Mgh \sin \theta dt, \\ OS &= OS' = Cn, \\ SQ &= S'Q' = A\dot{\psi} \sin \theta, \\ &\angle SKS' = \dot{\psi}dt, \\ &\angle SVS' = \dot{\psi}dt \cos \theta, \\ &\angle SOS' = \dot{\psi}dt \sin \theta. \end{aligned}$$

Also if $Q'S''$ be drawn parallel to QS,

$$\begin{aligned} SS' = SS'' + S''S' &= QQ' + Q'S' \sin S'Q'S''. \\ &= (Mgh \sin \theta)dt + (A\dot{\psi} \sin \theta)(\dot{\psi} \cos \theta dt). \end{aligned}$$

But $SS' = OS \angle SOS' = Cn\dot{\psi} \sin \theta dt$.

Whence, equating the two values of SS', and cancelling the common factors we find

$$(Cn - A\dot{\psi} \cos \theta)\dot{\psi} = Mgh,$$

the well-known quadratic for steady precession, usually obtained in less simple ways.

Consider now the relations involved in the elementary triangles VQQ' and VSS' remembering that the angles at V are all infinitesimal; and make a new diagram (Fig. 3, *a* and *b*) in which the plane of these figures is the plane of the paper, the same letters being used for the same points

[1] Greenhill, Notes on Dynamics. Greenhill, Report on Gyroscopic Theory, Chap. I., §§ 3 et sqq. Gray and Gray, Treatise on Dynamics, § 271.

[2] Some have condemned this use of the element of time dt, apparently on the ground that, as the motion is strictly oscillatory, the value of θ must, in general, change during this time. Perhaps these writers would consent to the employment of the symbol Δt with the proviso that it denote an integral number of the periods of the motion. This would still be a small time as the period is very short in the cases to which the above considerations are applicable. The vectors representing the change in the angular momentum still give the integral impulse over the time taken. This surely is an unnecessary refinement, for when the precession is approximately steady the period is very small and the amplitude negligible.

as in Fig. 2. Take A as the mid point of VS, and denote the distance AQ by x and VS by L

$$QQ' = VQ \angle QVQ' = (VA + AQ) \angle QVQ'$$

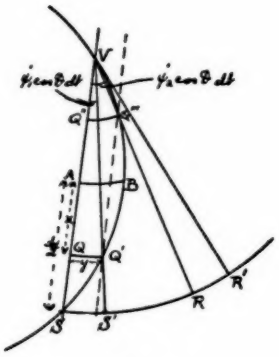

Fig. 3, *a*.

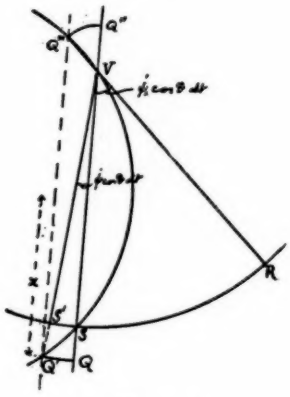

Fig. 3, *b*.

$$= \left(\frac{L}{2} + x\right)(\psi \cos \theta dt)$$

$$= (Mgh \sin \theta)dt, \text{ as before.}$$

Hence

$$\left(\frac{L}{2} + x\right)(\psi \cos \theta) = Mgh \sin \theta \tag{1}$$

Also

$$QS = \left(\frac{L}{2} - x\right) = A\psi \sin \theta \tag{2}$$

From these, by multiplication,

$$\frac{L^2}{4} - x^2 = AMgh \tan \theta \sin \theta \tag{3}$$

$$= A \tan \theta \frac{QQ'}{dt}.$$

Hence

$$\frac{QQ'}{dt} = y = \frac{\frac{L^2}{4} - x^2}{A \tan \theta}.$$

Or, substituting (see Fig. 2) $L = Cn \tan \theta$,

$$\frac{C^2n^2 \tan \theta}{4A} - y = \frac{x^2}{A \tan \theta}.$$

In view of the fact that, due to the short time dt, the arcs QQ', etc., may

be treated as short straight lines perpendicular to VS, this equation exhibits the locus of Q', for constant θ, as a parabola passing through the points V and S, with its vertex opposite A, ($x = 0$) at a distance ($C^2n^2 \tan \theta/4A$). Thus for a given value of the applied couple ($Mgh \sin \theta$, represented by the distance of the dotted line from VS) we find two solutions corresponding to the two points common to the curve and the dotted line. These give the two possible steady precessions at angle θ for the same applied couple; ψ_1 proportional to the angle SVS', and ψ_2 proportional to the angle SVR, as either of these angles is swept out in the same small time dt.

Further it is obvious, from the nature of the curve, that an increase in the applied couple brings both Q' and Q''' towards the vertex B, increasing the lower value of the precession, *i.e.*, increasing the angle SVS', and decreasing the value of the higher precession, *i.e.*, decreasing the angle SVR. With still greater increase in the applied couple these points (Q', Q''') finally meet at the vertex B for which condition, by putting x equal to zero in equation 1 we find the limiting value

$$Mgh \sin \theta_{x=0} = \frac{L}{2} \psi \cos \theta ,$$

or inserting $L = VS = Cn \tan \theta$. (See Fig. 1.)

$$= \frac{Cn}{2} \psi \tan \theta, \cos \theta.$$

Or from equation 3 in the same way

$$Mgh \sin \theta_{x=0} = \frac{C^2n^2 \tan \theta}{4A}.$$

For values of the applied couple greater than this there is obviously no real solution and therefore no possible value for *steady* precession.

Now, following the changes in the opposite direction (of decreasing values of the applied couple) we are led, for zero couple, to zero precession for the lower value (Q' coinciding with S) and for the upper value (Q''' coinciding with V) to a precession given by

$$\psi_V = \frac{\angle SVR'}{\cos \theta dt}$$

(VR' being tangent to the curve at V) which is the free precession of Euler or the adynamic precession of Kelvin.

If the applied couple now becomes negative (Fig. 3*b*) we deal with points on the curve below S and above V. The lower precession changes

sign, having passed through zero, while the upper one continues to increase, having passed through the adynamic value.

From these characteristics of the change of the precession with change in the applied couple, the rise or fall of the axis of the top with a forced change in the magnitude of the free precession, follows in the usual way.

There is another way of indicating these changes, which while it gives a less vivid picture of the relations between them, yet gives exact values in place of the merely relative values of the other method. One notes from equation 2 that SQ and SQ'' represent the two values of $A\psi \sin \theta$. Thus

$$\psi_1 = \frac{SQ}{A \sin \theta}$$

and

$$\psi_2 = \frac{SQ''}{A \sin \theta},$$

so the values of the two precessions are given by the distances of Q and Q'' from S, whether these be positive or negative (*i.e.*, whether these points fall between S and V or are external to that segment. Further we see that since $x = AQ = AQ''$ that the sum of $SQ + SQ''$ is always SV, *i.e.*, the sum of the two velocities for steady precession is always that of the free or adynamic precession, $Cn/(A \cos \theta)$.

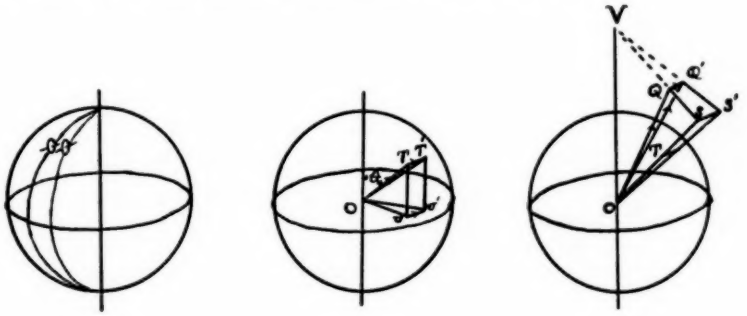

Fig. 4.

In the case of a rotating body in precession along a predetermined path, as, for instance, a flywheel with axis fixed with regard to a rotating earth, the general construction is the same. We should have a position diagram (Fig. 4, *a*) showing the positions of the rotating body at an interval of dt. Then the vector diagram (Fig. 4, *b*) where all points are lettered to correspond to those of Fig. 1, and where θ is the angle between the axes of the earth and of the flywheel. QQ' is the angular impulse required to change the resultant angular momentum OQ to the value

(OQ') it has dt later and the calculation follows as before. However as the angular velocity of the earth about its axis, ψ_e is so very small with respect to ω in the cases of chief interest (effort of flywheel to precess, couple on gyro-compass, etc.) the vectors TS and SQ, *i.e.*, $C\dot{\psi}_e \cos\theta$ and $A\dot{\psi}_e \sin\theta$, are ignored and the figure becomes that of Fig. 4 *c*, where $OT = OT' = C\omega$ and TT' (or UU') is the impulse $(C\omega \sin\theta\dot{\psi}_e)dt$. Hence the couple required to prevent precession towards the pole of the earth is $C\omega\dot{\psi}_e \sin\theta$; the result usually obtained by more complex analysis. The couple on a gyro-compass is simply the vertical component of this couple at the place in question.

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QUEENS UNIVERSITY,
KINGSTON, ONT.,
September 5, 1921.

THE PATH OF A RIGID ELECTRON WHICH MOVES IN A MAGNETIC FIELD OF CONSTANT STRENGTH ROTATING WITH CONSTANT ANGULAR VELOCITY.

BY E. O. HULBURT.

SYNOPSIS.

Equations of Motion of a Rigid Electron in a Uniformly Rotating Magnetic Field of constant strength rotating with a frequency $\omega/2\pi$ in the XZ plane, are obtained. The reactions on the motion due to finite size, radiation, and the variation of mass with velocity are neglected. If initially the velocity of the electron has components only along the X-axis or the Z-axis the path of the electron is a wavy curve inside an annular space whose axis is parallel to the Y-axis. If the initial velocity of the electron has components only along the Y-axis the path is a rather complicated type of spiral winding in the general direction of the Y-axis. It is found that a high frequency of rotation of the magnetic field, of the order of 10^6, such as may be produced by means of electron-tube circuits, would not impart a great velocity to the electron.

1. A rigid electron is assumed of mass m and charge e and of size small in comparison with the displacements it undergoes. The electron is subjected to a magnetic field whose components are H_x, H_y and H_z. The reactions on its motion due to the variation of mass with velocity and to radiation both from the electron and from the magnetic field are neglected. Let x, y and z be the positional coördinates of the electron. When electromagnetic units are used, the equations of motion of the electron are, in Newtonian notation,

$$\begin{aligned} \frac{m}{e}\ddot{x} &= H_y\dot{z} - H_z\dot{y}, \\ \frac{m}{e}\ddot{y} &= H_z\dot{x} - H_x\dot{z}, \\ \frac{m}{e}\ddot{z} &= H_x\dot{y} - H_y\dot{x}. \end{aligned} \tag{1}$$

Let H rotate in the XZ plane with a constant angular velocity of frequency $\omega/2\pi$. Then

$$H_x = H\cos\omega t, \qquad H_y = 0, \qquad H_z = H\sin\omega t. \tag{2}$$

Introducing (2) into (1) gives

$$\begin{aligned} \frac{m}{e}\ddot{x} &= -H\dot{y}\sin\omega t, \\ \frac{m}{e}\ddot{y} &= H(\dot{x}\sin\omega t - \dot{z}\cos\omega t), \\ \frac{m}{e}\ddot{z} &= H\dot{y}\cos\omega t. \end{aligned} \tag{3}$$

These equations may be integrated and the constants of integration determined from the initial conditions.

2. Suppose initially that when $t = 0$, $x = y = z = \dot{x} = \dot{y} = 0$ and $\dot{z} = w$. The solutions[1] of (3) are in this case,

$$\begin{aligned} x &= \frac{wH^2e^2}{2\nu m^2}\left[\frac{\cos(\nu+\omega)t}{(\nu+\omega)^2} - \frac{\cos(\nu-\omega)t}{(\nu-\omega)^2}\right] + \frac{2\omega w m^2}{H^2e^2}, \\ y &= \frac{wHe}{\nu^2 m}[\cos\nu t - 1], \\ z &= \frac{wH^2e^2}{2\nu m^2}\left[\frac{\sin(\nu+\omega)t}{(\nu+\omega)^2} + \frac{\sin(\nu-\omega)t}{(\nu-\omega)^2}\right], \end{aligned} \tag{4}$$

where

$$\nu = \sqrt{\frac{H^2e^2}{m^2} + \omega^2}.$$

To reduce to the case of a stationary magnetic field, ω is placed equal to zero in (2) and (4). Then $\nu = He/m$, $H_x = H$, $H_y = H_z = 0$, and (4) becomes

$$\begin{aligned} x &= 0, \\ y &= \frac{wm}{He}\left(\cos\frac{He}{m}t - 1\right), \\ z &= \frac{wm}{He}\sin\frac{He}{m}t. \end{aligned} \tag{5}$$

We see from (5) that the electron moves in a circle in the YZ plane of radius wm/He and with the centre at $(0, -wm/He, 0)$. This is in agreement with formulas given by others.[2]

3. The determination of the path of the electron from equations (4) is facilitated by noticing that

$$\sqrt{\left(x - \frac{2\omega w m^2}{H^2e^2}\right) + z^2} = \frac{wH^2e^2}{2\nu m^2}\sqrt{\frac{1}{(\nu+\omega)^4} + \frac{1}{(\nu-\omega)^4} - \frac{2\cos\nu t}{(\nu^2-\omega^2)^2}}. \tag{6}$$

[1] I am indebted to Dr. E. W. Chittenden of the Mathematics Department for these solutions.

[2] J. J. Thomson, Conduction of Electricity through Gases, page 107, 1906.

This transformed to polar coördinates is

$$\rho = \sqrt{a + b \cos 2\nu t}, \tag{7}$$

where ρ, a and b are determined by identifying (7) with (6). From (7) it follows that at no time does ρ become greater than $\sqrt{a+b}$ or less than $\sqrt{a-b}$. Hence the electron moves always between two coaxial cylindrical surfaces of radii $\sqrt{a+b}$ and $\sqrt{a-b}$, the axis of the surfaces being parallel to the Y-axis. The equation of the axis is

$$x = \frac{2\omega w m^2}{H^2 e^2},$$

$$z = 0.$$

Further, from (4) it is seen that y varies harmonically with the time reaching the extreme values 0 and $-2\omega \times He/\nu^2 m$. Therefore the electron moves always between the two planes $y = 0$ and $y = -2\omega He/\nu^2 m$. With these facts in mind it is found that the electron pursues a wavy orbit inside the annular space as indicated in Fig. 1. The electron does not in general retrace its path during its subsequent excursion through the space to which it is confined.

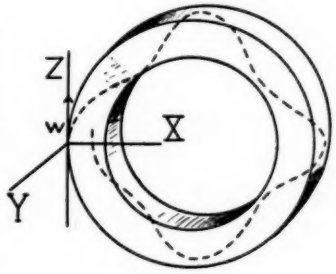

Fig. 1.

The case in which the electron has initial velocity components only along the X-axis is by symmetry the same as the case just discussed, and the path of the electron is of the same form as that of Fig. 1.

4. If the initial conditions are $t = 0$,

$$x = y = z = \dot{x} = \dot{z} = 0, \text{ and } \dot{y} = v,$$

the solutions of (4) are:

$$x = \frac{vH^3e^3}{2\nu^2m^3}\left[\frac{\sin(\nu+\omega)t}{(\nu+\omega)^2} - \frac{\sin(\nu-\omega)t}{(\nu-\omega)^2}\right] + \frac{vHe}{\nu^2 m}\sin\omega t,$$

$$y = \frac{vH^2e^2}{\nu^3m^2}\sin\nu t + \frac{v\omega^2}{\nu^2}t, \tag{8}$$

$$z = -\frac{vH^3e^3}{2\nu^2m^3}\left[\frac{\cos(\nu+\omega)t}{(\nu+\omega)^2} + \frac{\cos(\nu-\omega)t}{(\nu-\omega)^2}\right] - \frac{vHe}{\nu^2 m}\cos\omega t + \frac{2\nu m}{He}.$$

The path of the electron is found by transforming equations (8) to a new set of axes X', Y', Z', such that the new coördinates x', y', z', are

related to the old ones x, y, z by the relations

$$x' = x - \frac{vHe}{v^2m}\sin \omega t,$$

$$y' = y - \frac{v\omega^2}{v^2}t,$$

$$z' = z + \frac{vHe}{v^2m}\cos \omega t - \frac{2vm}{He}.$$

The new axes remain always respectively parallel to the old ones. The new origin moves on a spiral wound on a cylinder, circumventing the cylinder $\omega/2\pi$ times a second and advancing with a velocity whose Y-component is $v\omega^2/v^2$. The radius of the cylinder is vHe/v^2m; the equation of its axis is

$$x = 0,$$

$$z = \frac{2vm}{He}.$$

With reference to the new axes the path of the electron is of the same form as discussed in section (3). With reference to the old axes the path is a rather complicated type of spiral winding in the general direction of the Y-axis.

5. A special case occurs when ω is large. This is of interest because it is possible by means of electron tube circuits to produce magnetic fields which rotate with frequencies of the order of 10^6, although with the apparatus available at present such fields are relatively weak. If ω is large and if the initial conditions are those of section (2) we find that y, z, $\dot{x}$, $\dot{y}$, $\dot{z}$ are small and x is large. With the initial conditions of (3) and with ω large, x, z, $\dot{x}$, $\dot{z}$ are small, $y \doteq vt$ and $\dot{y} \doteq v$. We see from this that even when the magnetic field rotates at a high frequency the electron does not acquire a very great velocity.

STATE UNIVERSITY OF IOWA,
November, 1921.

THE THERMOPHONE.

By Edward C. Wente.

Synopsis.

Acoustic Efficiency of Thermophones of the Heated Foil or Wire Type.—Theoretical formulæ are derived for the maximum value of the alternating pressure produced within the enclosure of any thermophone when a given alternating current, superposed on a direct current, is passed through the central foil or wire. The effect of certain simplifying assumptions which are made is shown to be small in practical cases. As an *experimental verification* of the formulæ, an electrostatic transmitter was calibrated for a wide range of frequencies with four thermophones which differed greatly in their physical constants, the formulæ being used to compute the pressures produced. The four calibrations thus obtained agree with each other closely and also with an independent calibration made with a pistonphone.

Methods of Calibrating Acoustical Transmitters.—In addition to the pistonphone, the thermophone is now available. The circuits used in calibrating an electrostatic transmitter are given.

Method of Measuring the Thermal Conductivity of a Gas by Using a Thermophone is Suggested.—It would have the advantage of avoiding difficulties due to convection.

In a paper on the theory of the thermophone, Arnold and Crandall[1] have developed formulæ for the absolute value of its acoustical efficiency as a function of the frequency. While these formulæ are sufficiently accurate for most practical purposes, certain discrepancies[2] have been observed, which cannot be attributed to experimental errors. In order to use the thermophone for calibrating acoustical apparatus throughout a wide range of frequencies it has therefore been necessary to make a more detailed analysis of its action.

In this paper formulæ are derived for the efficiency of a thermophone with a heating element of metal foil, which are found to agree closely with such experimental tests as it has been possible to apply. Expressions for the efficiency of the thermophone having a wire heating element are also obtained by the same method of analysis. Only those cases are considered in which the thermophone heating element is located within an enclosure the linear dimensions of which are small in comparison with the wave length of sound. When the element is not placed within a small enclosure the thermophone is of little importance as a precision instrument. Its sound output is not only small but indefinite in most practical cases. Since the sound waves are generated by the alternate expansion and contraction of a layer of air in the immediate

[1] Phys. Rev., X, 22 (1917).

[2] Phys. Rev., X, 52 (1917).

neighborhood of the foil, the characteristics of the system are similar to those of a source of sound consisting of a diaphragm of small mass and stiffness actuated by a constant alternating force. The radiation resistance, which varies with the position of surrounding objects, may in this case be an appreciable part of the mechanical impedance of the system.

Equation of Thermal Equilibrium of an Ideal Gas.

The differential equation of heat conduction for a continuously varying temperature in a solid is well known. The corresponding equation for gases, which is made the basis of the following study of the action of the thermophone, is obtained by putting the rate of increase of heat content of an element of volume of the gas equal to the rate at which work is done upon it plus the heat received by conduction. We thus get

$$\rho c_v \frac{DT}{Dt} = -Ap\rho \frac{DV}{Dt} - K\nabla^2 T,$$

where $V = 1/\rho$ is the specific volume of the gas. Since for an ideal gas $p = \rho RT$ and $c_p - c_v = AR$, this equation reduces to

$$\rho c_p \frac{DT}{Dt} - A\frac{Dp}{Dt} - K\nabla^2 T = 0. \tag{1}$$

The loss by radiation is small in any practical case and so has been neglected.

Thermophone with Heating Element of Metal Foil.

Pressure Produced by a Periodic Change in Temperature of a Metal Strip Within a Small Enclosure.—If the temperature of the foil varies periodically, a temperature wave will be set up in the medium surrounding the foil. At acoustic frequencies these waves are attenuated to a small fraction of their original amplitude at distances small compared with the dimensions of the foil. Hence, in this discussion these thermal waves may be regarded as plane waves; also, since the fluid velocity is small, D/Dt is very nearly equal to $\partial/\partial t$. If then the temperature of the strip is given by $\Theta_0 + \Theta_1 e^{i\omega t}$, where Θ_1 is small compared with Θ_0, and if second order effects are neglected,

$$T = T_0 + T_1 e^{i\omega t},$$
$$p = p_0 + p_1 e^{i\omega t},$$
$$\rho = \rho_0 + \rho_1 e^{i\omega t},$$

and from (1) it follows that

$$\rho_0 c_p i\omega T_1 - Ai\omega p_1 - K\frac{\partial^2 T_1}{\partial x^2} = 0. \tag{2}$$

In the solution of this equation ρ_0 and K may be assigned the values that obtain at the temperature of the foil, since at points near the foil the gas has approximately the same temperature as the foil itself. If the dimensions of the enclosure are small compared with a wave-length of sound, p_1 is independent of x. The complete solution of (2) then is

$$T_1 = Ce^{\sqrt{2i}\alpha x} + De^{-\sqrt{2i}\alpha x} + \frac{k-1}{k}\frac{\Theta_0}{p_0}p_1,$$

in which α is set equal to $\sqrt{\frac{\rho_0 \omega c_p}{2K}}$, and k is the ratio of the specific heats.

The boundary conditions require that for $x = \infty$, T_1 shall not be ∞ and for $x = 0$, T_1 shall equal Θ_1. Hence,

$$T_1 = \left(\Theta_1 - \frac{A\omega p_1}{2\alpha^2 K}\right)e^{-\sqrt{2i}\alpha x} + \frac{k-1}{k}\frac{\Theta_0}{p_0}p_1. \tag{3}$$

Also

$$p_1 = \frac{2p_0 a}{T_a V_0}\int_0^{V_0/2a} T_1 dx,^1 \tag{4}$$

where V_0 is the volume, and T_a the mean temperature of the gas in the enclosure. Since, in all practical cases, $e^{-V_0\alpha/2a}$ is small compared with unity, it follows from (3) and (4) that

$$\Theta_1 = \frac{k-1}{k}\frac{\Theta_0}{p_0}\left[1 - \left(1 - \frac{k}{k-1}\frac{T_a}{\Theta_0}\right)\frac{V_0\alpha}{2a}(1+i)\right]p_1. \tag{5}$$

This equation gives the periodic pressure within the enclosure in terms of the periodic temperature variation of the heating element. The problem remains to express Θ_1 in terms of quantities that can be measured directly.

Temperature of the Heating Element.—Consider the case in which the thermophone element is heated by both direct and alternating currents, *i.e.*, by a current equal to $I_0 + I_1 \cos \omega t$ amperes. If I_0 is large compared with I_1, the rate at which heat is developed in the foil is approximately equal to the real part of

$$0.239RI_0^2 + 0.478RI_0I_1e^{i\omega t} \text{ calories per second.}$$

Equating this value to the rate with which heat is lost by radiation and conduction plus the rate with which it is stored in the foil, we get for the fundamental frequency

$$04.78RI_0I_1 = 8aC\Theta_0^3\Theta_1 - 2aK\left(\frac{\partial T}{\partial x}\right)_{x=0} + a\gamma i\omega\Theta$$

$$= \Theta_1(a\gamma i\omega + 2a\alpha K\sqrt{2i} + 8aC\Theta_0^3) - \frac{Aa\omega\sqrt{2i}}{\alpha}p_1, \tag{6}$$

[1] See Arnold and Crandall, PHYS. REV., N.S., Vol. X, 32 (1917).

where C is the radiation constant of the foil and γ is the heat capacity per unit area of foil. Reintroducing the time factor and retaining only the real part, we get finally from (5) and (6) for the pressure developed within the enclosure,

$$p_1' = \frac{0.478 R I_0 I_1 \cos(\omega t - \Phi)}{\left[\left(GQ - RF - \frac{Aa\omega}{\alpha}\right)^2 + \left(FQ + RG - \frac{Aa\omega}{\alpha}\right)^2\right]^{1/2}}, \qquad (7)$$

where

$$F = \frac{V_0 \alpha T_a}{2ap_0}\left(1 - \frac{k-1}{k}\frac{\Theta_0}{T_a}\right),$$

$$G = \frac{V_0 \alpha T_a}{2ap_0}\left[1 - \frac{k-1}{k}\frac{\Theta_0}{T_a}\left(1 - \frac{2a}{\alpha V_0}\right)\right],$$

$$Q = 2a\alpha K + 8aC\Theta_0^3,$$

A = area of one side of strip

$$R = a\gamma\omega + 2a\alpha K,$$

$$\Phi = \tan^{-1}\frac{FQ + GR - \frac{Aa\omega}{\alpha}}{GQ - RF - \frac{Aa\omega}{\alpha}}.$$

In these expressions α and K must be assigned values corresponding to the temperature of the foil. If K_0 and α_0 are the values at 0° C., then

$$K = K_0\left(\frac{\Theta_0}{273}\right)^{1/2}; \qquad \alpha = \alpha_0\left(\frac{273}{\Theta_0}\right)^{3/4}.$$

The Thermophone with Cylindrical Heating Element.

For laboratory purposes it is generally more practicable to use a thermophone with a heating element of metal foil instead of Wollaston wire as proposed by DeLange.[1] However, there are some cases in which the latter is of value as a standard source of sound, particularly in measurements on ear sensitivity. Thermophones of this type can readily be placed within the ear passage. Complications arising from stationary waves are thus almost entirely eliminated.

Pressure Within an Enclosure Containing a Cylindrical Wire of Variable Temperature.—Consider an airtight cylindrical enclosure along the axis of which is placed a wire of small diameter, having a temperature which can be represented by the expression $\Theta_0 + \Theta_1 e^{i\omega t}$. As before, the fluid velocity in the surrounding medium is small so that the relation (1) reduces to

$$K\left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r}\right) + A\frac{\partial p}{\partial t} - c_p\rho\frac{\partial T}{\partial t} = 0. \qquad (8)$$

[1] Proc. Royal Soc., 91A, p. 239 (1915).

For the equation corresponding to (2) we have

$$\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} - 2i\alpha^2\right) T_1 = -\frac{i\omega A p_1}{K}. \tag{9}$$

If, as before, α is assumed to be constant, the complete solution of (9) is

$$T_1 = AJ_0(\sqrt{-2i}\alpha r) + BH_0(\sqrt{-2i}\alpha r) + \frac{k-1}{k}\frac{\Theta_0}{p_0}p_1.^1$$

The boundary conditions require that, as r approaches ∞, T_1 shall not approach ∞, and when r is equal to a, the radius of the wire, T_1 shall be equal to Θ_1. Hence

$$T_1 = \frac{\left(\Theta_1 - \frac{k-1}{k}\Theta_0\frac{p_1}{p_0}\right)}{H_0^{(2)}(\sqrt{-2i}\alpha a)} H_0^{(2)}(\sqrt{-2i}\alpha r) + \frac{k-1}{k}\Theta_0\frac{p_1}{p_0} \tag{10}$$

corresponding to (4) we have in this case the relation:

$$p_1 = \frac{p_0 l}{T_a V_0}\int_a^R T_1 2\pi r dr, \tag{11}$$

where R is the radius of the cylindrical enclosure, and l the length of the wire. In any practical type of thermal receiver R is large compared with a, and $aH_1^{(2)}(\sqrt{-2i}\alpha a)$ is large compared with $RH_1^{(2)}(\sqrt{-2i}\alpha R)$, so that to a close approximation we have from (10) and (11)

$$p_1 = \frac{2p_0\pi a l\left(\frac{k-1}{k}\frac{\Theta_0}{p_0}p_1 - \Theta_1\right)H_1^{(2)}(\sqrt{-2i}\alpha a)}{\sqrt{-2i}\alpha V_0\left(T_a - \frac{k-1}{k}\Theta_0\right)H_0^{(2)}(\sqrt{-2i}\alpha a}. \tag{12}$$

Temperature of the Heating Element.—Setting the rate with which heat is supplied to the wire equal to the rate with which heat is lost by conduction and radiation plus the rate with which heat is stored, we obtain the following relation

$$0.478RI_0I_1 = l\left[-2\pi aK\left(\frac{\partial T}{\partial r}\right)_{r=a} + 8\pi aC\Theta_0^3\Theta_1 + \gamma' i\omega\right]$$
$$= l\left[\gamma' i\omega\Theta_1 + 2K\pi\frac{\sqrt{-2i}\alpha a H_1^{(2)}(\sqrt{-2i}\alpha a)}{H_0^{(2)}(\sqrt{-2i}\alpha a)}\left(\Theta_1 - \frac{\omega A p_1}{2\alpha^2 K}\right) + 8\pi aC\Theta_0^3\Theta_1\right], \tag{13}$$

[1] The notation here used for the Bessel functions is the same as given in Jahnke and Emde, "Functionen-tafeln," p. 90 ff.

where γ' is the heat capacity per unit length of the wire. Let

$$\frac{H_0^{(2)}(\sqrt{-2i\alpha a})}{H_1^{(2)}(\sqrt{-2i\alpha a})} = M + iN.$$

We then get from (12) and (13)

$$0.478RI_0I_1 = \left[(\gamma' i\omega + 8\pi aC\Theta_0^3)\left(\frac{k-1}{k}\frac{\Theta_0}{p_0}l - \frac{(1-i)\left(T_a - \frac{k-1}{k}\Theta_0\right)V_0}{2p_0\pi a}(M+iN)\right) + \frac{2i\alpha^2 KV_0\left(T_a - \frac{k-1}{k}\Theta_0\right)}{p_0}\right]p_1. \tag{14}$$

In general, $8\pi aC\Theta_0^3$ is small compared with $\gamma'\omega$. For example, in the case of a thermophone having a wire heating element, 0.0003 cm. in diameter, for a frequency of 25 cycles per second and $\Theta_0 = 800°$ absolute, the error, introduced by neglecting $8\pi aC\Theta_0^3$ in (14), even for these extreme conditions, is only 4 per cent. If then $8\pi aC\Theta_0^3$ is neglected, we obtain finally for the real part of p_1, the alternating pressure developed within the enclosure,

$$p_1' = \frac{0.956\pi a p_0}{\left(T_a - \frac{k-1}{k}\Theta_0\right)\alpha V_0\omega\gamma'}\frac{RI_0I_1\cos(\omega t - \Phi)}{\left[(N-M)^2 + \left(\frac{k}{k-1}\frac{2\pi aAp_0}{\alpha\Theta_0\gamma'} + \frac{2\pi al}{V_0\alpha\left(\frac{k}{k-1}\frac{T_a}{\Theta_0} - 1\right)} - (M+N)\right)^2\right]^{1/2}}, \tag{15}$$

where

$$\Phi = \tan^{-1}\frac{\left[\frac{k}{k-1}\cdot\frac{2\pi aAp_0}{\alpha\Theta_0\gamma'} + \frac{2\pi al}{V_0\alpha\left(\frac{k}{k-1}\frac{T_a}{\Theta_0} - 1\right)} - (M+N)\right]}{N-M}.$$

In the calculation of the values of $N - M$ and $M + N$ for small values of αa, it is convenient to use the following approximation formulæ,

$$N - M = 2\alpha a\left[\log_e\frac{\alpha a}{\sqrt{2}} + 0.577\right]; \qquad N + M = \frac{\alpha a}{2}.$$

These formulæ are correct to within a few per cent. for values of αa even as large as 0.15. For larger values of αa, M and N may be calculated from the tables given in Jahnke and Emde's "Functionentafeln" pp. 139–140. $H_\nu^{(2)}(\sqrt{-iX})$ is the conjugate complex quantity of $H_\nu^{(1)}(\sqrt{iX})$.

Values for the maximum pressure developed have been calculated by the above formulæ for thermophones having the following constants.

I. Heating element of metal foil: volume of the enclosure = 14 cu. cm., thickness of the gold foil = 0.79×10^{-5} cm., area of the gold foil = 5.5 sq. cm., $\Theta_0 = 335°$ absolute, $T_a = 300°$ absolute.

II. Heating element of Wollaston wire: volume of the enclosure = 1 cu. cm., diameter of the wire = 0.0003 cm., length of the wire = 1 cm., $T_a = 300°$ absolute, $\Theta_0 = 335°$ absolute.

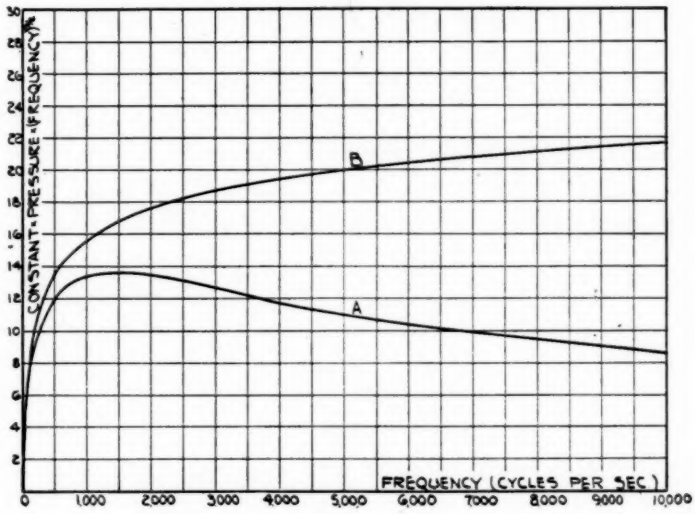

Fig. 1.

Frequency characteristics of thermophones.

A. Cylindrical heating element.

B. Flat-strip heating element.

In Fig. 1 the products of pressure and the 3/2 power of the frequency are plotted as a function of frequency. The curves thus show the amount of deviation from a simple 3/2 power relation. It appears that as telephone receivers the two types of instruments produce approximately the same amount of distortion and so neither possesses an advantage in this regard.

In the preceding analysis the heating element was assumed to lie along the axis of a cylindrical enclosure. But since the temperature

waves emanating from the wire have a large attenuation and a short wave length, the equations apply without alteration to any case in which the wire is located near the central part of the enclosure.

FURTHER CONSIDERATIONS OF THE FORMULÆ.

In the preceding discussion the following assumptions have been made: The walls of the enclosure are non-conductors of heat, the temperature of the foil has the same value throughout its entire length, and at the surface of the foil the gas has the same temperature as the foil itself. Although for most practical cases these assumptions do not introduce inaccuracies of any consequence into the formulæ, the order of magnitude of the errors will here be considered.

If the walls are perfect conductors, as is approximately true in most cases, it may be shown that a first order correction is obtained by multiplying (7) by

$$\sqrt{1 - \frac{S}{V_0\alpha} + \frac{S^2}{2V_0^2\alpha^2}},$$

where S is the area of the walls of the enclosure. This factor is in general nearly unity.

In practice, the ends of the foil are held between comparatively massive clamps, so that almost no temperature variation at these points is produced by the alternating current. To take account of this fact the values of p_1' as given by equations (7) and (15) should be multiplied by

$$\sqrt{1 - \frac{2}{\alpha' l} + \frac{2}{(\alpha' l)^2}},$$

where l is the length of the element and α' is the value of α for the heating element. It may be shown that this factor gives the correction to the first order and is in general also nearly equal to unity.

When heat flows from a solid wall to a gas, the temperature corresponding to the velocity with which a molecule leaves the wall after a single impact will not be the same as the temperature of the wall. This fact is equivalent to a temperature drop between the solid and the gas.[1] This temperature drop at the surface of the foil is given by

$$\Delta\Theta = -\gamma\left(\frac{\partial T}{dx}\right)_{x=0},$$

where γ is a constant depending on the gas and its mean free path and on the condition of the surface of the solid wall. For hydrogen and a

[1] Kundt and Warburg, Pogg. Ann., 156, p. 177 (1875).

smooth solid surface on platinum it is equal to 7.25λ,[1] where λ is the mean free path of the molecules of the gas. For normal atmospheric conditions we find in this case to a first approximation $\Delta\theta_1 = 3 \times 10^{-4} f^{1/2}\theta_1$. For a frequency as high as 10,000 cycles this is only $0.027\theta_1$ or less than 3 per cent. of the maximum value of the periodic temperature of the foil. For all practical purposes, therefore, the temperature drop at the surface of the foil may be disregarded.

Experimental Verification of the Theory of the Thermophone with Heating Element of Metal Foil.

(*a*) *Comparison of Thermophones having Different Physical Constants.*—There appears to be no way in which the pressure produced by a thermophone within an enclosure can be measured over its useful frequency range. The validity of equation (7), therefore, cannot be tested in a direct way. However, the alternating pressure exerted on the diaphragm of an electrostatic transmitter by thermophones having different physical constants may be compared. Whatever the sensitivity of an electrostatic transmitter as a function of frequency may be, it does not vary appreciably with time. Thus it is possible to determine at a number of fixed frequencies whether the alternating pressure varies with the different physical constants in accordance with equation (7). Experiments to this end have been carried out for a wide range of frequencies.

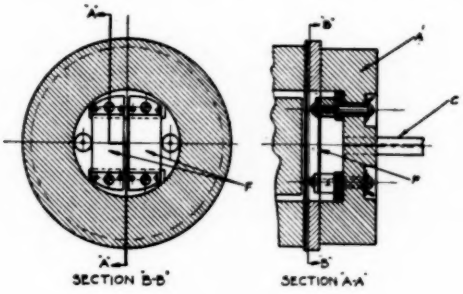

Fig. 2.

Thermophone in place for calibrating an electrostatic transmitter.

The thermophone was placed in front of the electrostatic transmitter in the manner shown in Fig. 2. The face of the transmitter together with the brass block, *A*, form an enclosure in which the heating elements, *F*, are centrally located. The enclosure is airtight except for the two equal capillary tubes, *C*. By means of these tubes gas is passed at a slow rate through the enclosure. To keep the pressure at atmospheric value, the pressure head on the intake tube is made equal to the suction

[1] S. Weber, A.d.P., 54, 439 (1917).

head on the outlet tube. These capillary tubes have a high impedance to the transmission of sound waves so that they do not affect the magnitude of the alternating pressure within the enclosure.

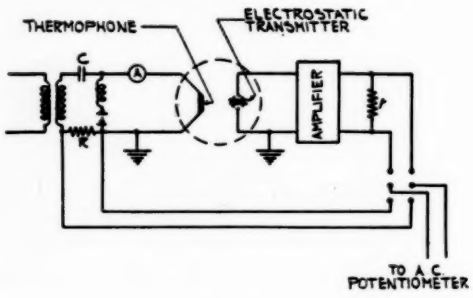

Fig. 3.

Circuit for calibrating an electrostatic transmitter with a thermophone.

The circuit used in the measurements is shown in Fig. 3. The ratio of the alternating potential drop across r and R was determined with an *a.c.* potentiometer.[1] This ratio multiplied by R and divided by the amplification of the amplifier gives the ratio of the voltage generated by the electrostatic transmitter to the alternating current passing through the thermophone heating element. The voltage per unit of pressure was then calculated by equation (7). Measurements were made with platinum foil, 6.81×10^{-5} cm. $\times$ 1.0 cm. $\times$ 5.35 cm., within an enclosure of 25.25 cu. cm. capacity, and with gold foil, 7.85×10^{-6} cm. $\times$ 1.0 cm. $\times$ 5.5 cm., within an enclosure of 13.9 cu. cm. capacity, both with hydrogen and with air within the enclosure. The conductivity of air was taken as 5.68×10^{-5} and of hydrogen, 41.6×10^{-3} c.g.s. units.

The values of voltage per dyne pressure as obtained with these thermophones for a particular electrostatic transmitter are given in the following table.

TABLE I.

Frequency	Gold Foil in Hydrogen.	Gold Foil in Air.	Platinum in Air.	Platinum in Hydrogen.
Cycles per sec.				
60	6.75		6.75	
300	4.85	5.00	4.82	
600	4.40	4.45	4.47	4.47
1000	4.20	4.30	4.45	4.30
2000	4.06	4.20		4.25
4000	4.40			4.55

[1] E. C. Wente, A Vacuum-Tube Alternating Current Potentiometer, Journal of the A.I.E.E., 40, p. 900, December, 1921.

It is seen from this table that the different thermophones yield practically the same results. Observations were not extended over the whole frequency range for each thermophone, since equation (7) applies only for a limited region. The frequency must be lower than the resonant frequency of the enclosure, and the wave length of the temperature wave emanating from the foil must be small compared with the dimension of the enclosure.

At the lower frequencies the predominating quantity in the denominator of equation (7) for gold in hydrogen is $2\alpha K$, while for platinum in air it is $\gamma\omega$. The tests, therefore, cover extreme conditions. Hence the fact that the values obtained with the different thermophones lie very near together is evidence for the correctness of equation (7), on the basis of which they were determined.

(*b*) *Comparison with a Pistonphone.*—If at some part of the frequency range it is possible to determine by an independent method the sensitivity of the electrostatic transmitter, a more direct experimental check of formula (7) can be obtained. Measurements were made on the electrostatic transmitter similar to those just described but with the thermophone replaced by a pistonphone. The construction of this apparatus is shown in Fig. 4. This pistonphone is similar to that described in a

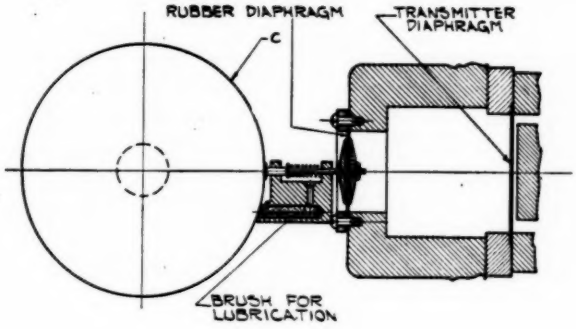

Fig. 4.

Use of pistonphone for calibrating an electrostatic transmitter.

former paper,[1] except that a cam, *C*, is used, which is cut so that with uniform rotation, a simple harmonic motion of 2 cycles per revolution is imparted to the piston. The pressure exerted on the diaphragm is given by

$$\frac{kp_0\sigma\xi\cos\omega t}{V_0}\sqrt{1-\frac{S}{V_0\alpha}+\frac{S^2}{2V_0^2\alpha^2}}, \qquad 16)$$

[1] E. C. Wente, PHYS. REV., X, p. 48 (1917).

where σ is the effective area of the face of the piston,
S is the area of the walls of the enclosure,
$\xi \cos \omega t$ is the displacement of the piston.

The last factor in (16) takes account of the fact that, due to the heat conduction of the walls, the compression does not take place quite adiabatically.

A diagram of the circuit used in this test is shown in Fig. 5. If the electrostatic capacities of the transmitter and voltmeter are known, the open-circuit voltage of the transmitter may be determined from the voltmeter readings. Measurements were made for frequencies ranging from 10 to 200 cycles per second. The open-circuit voltages per dyne pressure are plotted in Fig. 6 together with values obtained for the same electrostatic transmitter with a gold leaf-hydrogen thermophone. The points are seen to lie very near together. This fact shows that for this frequency range the absolute value of the pressure produced by the thermophone as a function of frequency is correctly given by equation (7). At the lower frequencies the pressure produced by the thermophone varies with the different factors entering into the

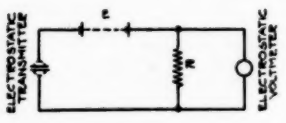

Fig. 5.

Circuit for calibrating electrostatic transmitter with pistonphone.

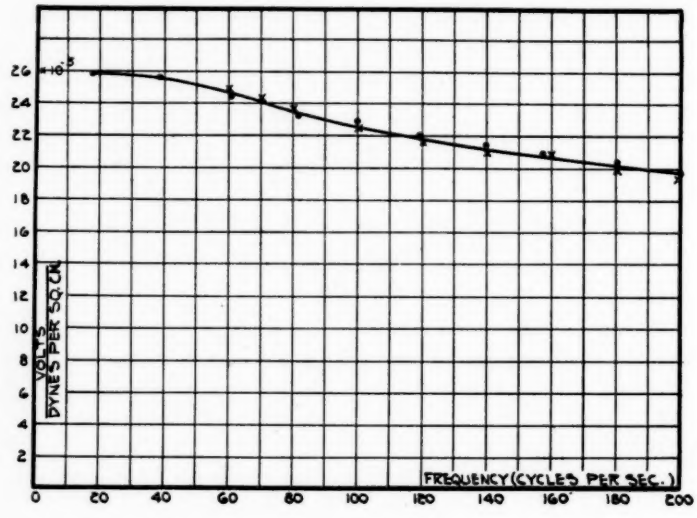

Fig. 6.

Efficiency of electrostatic transmitter.
•Values obtained with the pistonphone.
× Values obtained with the thermophone.

expression (7) more than at the higher frequencies. Therefore, it is reasonable to assume that this expression also gives correct values at higher frequencies.

The Use of the Thermophone for Measurements of the Thermal Conductivity of Gases.

One cause of uncertainty in the measurements with the thermophone is the fact that the thermal conductivity of gases is not well known. For example, in the case of hydrogen good authority can be found for values which differ from each other as much as 15 per cent. The thermophone suggests itself as a possible method for determining the conductivity of a gas. The principal source of error in conductivity measurements as heretofore carried out lies in the transport of heat by convection currents. In the case of the thermophone this source of inaccuracy is entirely eliminated.

Various arrangements of the apparatus for carrying out thermal conductivity measurements with the thermophone could be suggested. Some independent method of measuring an alternating pressure or producing one of known magnitude is required. Apparatus of the pistonphone type is perhaps the simplest arrangement that could be devised for the purpose.

Research Laboratories of the
American Telephone and Telegraph Co.
and the Western Electric Co., Inc.,
November 1, 1921.

ATOMIC RADII. I.[1]

BY MAURICE L. HUGGINS.[2]

SYNOPSIS.

The Physical Meaning of Bragg's "Atomic Spheres" and "Atomic Radii."—W. L. Bragg's "atomic spheres" and "atomic radii," considered in the light of the Lewis theory of atomic and molecular structure, have a definite physical meaning. *The "atomic sphere" of an atom is its valence shell, and its "atomic radius" is the distance from atomic center to a group of electrons (usually an electronpair) in the valence shell.* This idea is applied to several crystals.

Bragg's Method of Calculating Atomic Radii not always Valid.—Bragg's assumption that the distance between two adjacent atomic centers equals the sum of their radii is often not valid, since in many cases the group of electrons constituting the bond does not lie on the line joining the atomic centers; in other words, the two atomic "spheres" overlap.

Factors Affecting the Atomic Radius.—The various factors affecting the distance from atomic nucleus to valence group—the atomic radius—are discussed, with examples.

COMPARISONS of molecular and atomic volumes, computed from measurements of the densities of crystals, have often been made. The volume allotted to each atom of a given element, however, is found to vary greatly in different crystals, and, aside from giving a rough idea of the periodic variation of the size of the atom with atomic number, such comparisons have not been of very great value.

The Meaning of "Atomic Radius."—Of much wider application is the idea of "atomic radii," concerning which W. L. Bragg has written[3] in the Philosophical Magazine. He assumes each atom to be a sphere, or at least to possess a certain "sphere of influence," the size of which is practically constant for a given element in all crystals; also that each atom is held in position by touching the atoms around it. On these assumptions the distance between the centers of two adjacent atoms is equal to the sum of their atomic radii.

In diamond, for instance, in which each carbon atom is equidistant from four others,[4] each atomic sphere just touches those around it, the points of tangency being oriented with respect to the center of the atom

[1] This article is an amplification of a paper presented before the Berkeley meeting of the American Physical Society, Aug. 4, 1921, the abstract of which appears in the PHYS. REV. (2), *18*, 333 (1921).

[2] Dupont Fellow in Chemistry, Univ. of California, 1921–22.

[3] Phil. Mag. (6), *40*, 169 (1920).

[4] Bragg and Bragg, X-Rays and Crystal Structure, G. Bell & Sons, 1918, p. 102.

as are the four corners of a regular tetrahedron with respect to its center. The radius of the carbon atom is then exactly half the distance between atomic centers.

One of the ideas at the foundation of modern organic chemistry is that of the tetrahedral orientation of the four bonds by which a carbon atom is usually connected to other atoms. These bonds have been identified by G. N. Lewis[1] with pairs of electrons. It is but a step further to assume that each of the points of tangency of Bragg's hypothetical atomic spheres represents a pair of electrons, whenever the number of electrons required for such an arrangement is equal to the number of valence electrons present in the crystal. This requirement is met in diamond, for each carbon atom, being tetravalent, supplies four valence electrons to the structure—one to each of the valence pairs around it.

Application to Crystals.[2]—In a crystal of sphalerite, ZnS,[3] each zinc atom is surrounded by four equidistant sulfur atoms, and each sulfur atom by four equidistant zinc atoms. Each sulfur atom, according to the Lewis theory of valence and atomic structure,[4] has six valence electrons, and we may assume that zinc, being divalent, has two. This gives an average of four per atom, as in diamond, and we may again assume electronpairs on the centerlines between adjacent atoms—at the points where atomic spheres touch. Here also there is a tetrahedron of pairs around each sulfur and each zinc atom, as would be expected from the Lewis theory and the author's extension of it to the heavier elements.[5]

In iron pyrites (FeS_2), according to Bragg,[6] each iron sphere touches six sulfur spheres and each sulfur sphere is tangent to three iron spheres and one sulfur sphere. If we assume, as before, that the points of tangency represent electronpairs, then there is an octahedron of pairs around each iron atom and a tetrahedron of pairs around each sulfur. There are fourteen electrons per FeS_2 group required for this arrangement, which is what we should expect from atomic theory, each iron supplying two valence electrons and each sulfur six.

In each of the foregoing crystals the electronpairs are on (or very near, in the case of FeS_2) the centerlines between atoms, and the distance between closest atoms equals the sum of their atomic radii. In many crystals this is not the case—the valence electrons are not on the center-

[1] J. Am. Chem. Soc., *38*, 762 (1916).

[2] The electronic structures of diamond, ZnS, FeS_2, $CaCO_3$, and many other crystals are given and discussed by the author in an article soon to be published in the J. Am. Chem. Soc.

[3] Bragg and Bragg, loc. cit., p. 97.

[4] Loc. cit.

[5] J. Am. Chem. Soc., "Electronic Structures of Atoms," soon to be published.

[6] Bragg and Bragg, loc. cit., p. 127; W. L. Bragg, loc. cit.

lines, the atomic spheres overlap, and atomic radii can not be computed by Bragg's method.

As examples may be mentioned crystals of the alkali halides and of many of the metals. Let us consider a crystal of sodium fluoride, NaF, for instance. According to the Lewis theory a neutral sodium atom possesses one and a neutral fluorine atom seven valence electrons. In a crystal of NaF, each sodium valence electron has passed into the valence shell of a fluorine atom, producing the charged Na^+ and F^- ions. The structure of these ions may be represented [1] as $[(+11)(2\times1)(4\times2)]^+$ and $[(+9)(2\times1)(4\times2)]^-$ respectively. Each ion consists of a nucleus of charge $(+11)$ or $(+9)$ surrounded by an inner shell of two electrons, (2×1), and an outer shell of four electronpairs, (4×2), arranged at the corners of a tetrahedron, of which the nucleus is the center.

It has been shown[2] that the Na^+ and F^- ions are disposed at alternate corners of a simple cubic lattice, each sodium being symmetrically surrounded by six fluorines and each fluorine by six sodiums. Now it is impossible for these ions to be placed in the crystal in such a way that there will be a pair of electrons on each of the centerlines between adjacent ions. The symmetry requirements are such that the electronpairs must be on the *diagonals* of the small cubes of the lattice, somewhat as represented in Fig. 1. In this figure, for simplicity, only the electron-

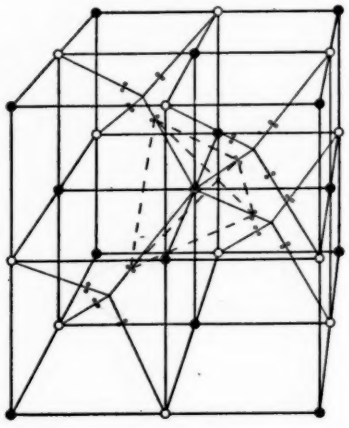

Fig. 1.

Arrangement of atomic centers and of sodium *or* fluorine electronpairs in NaF.

pairs in *one* kind of ion (Na^+ *or* F^-) are shown; those in the other are similarly placed, probably in the alternate cubes (left vacant in the diagram) of the structure.

[1] Huggins, "Electronic Structures of Atoms," loc. cit.

[2] Hull, Proc. Am. Inst. Elec. Eng., *38*, 1189 (1919). Davey, PHYS. REV. [2], *18*, 102 (1921).

The outer electronpairs of the ions in crystals of the other alkali halides are placed in a similar manner on the diagonals of the small cubes of the lattice. It is evident that in such structures as these, we are not justified in using Bragg's simple method of calculating atomic radii.

As a matter of fact, the atomic radius of sodium in a sodium fluoride crystal has very little meaning, unless we define it more explicitly. The sodium's only valence electron has gone into the valence shell of a fluorine atom. Should we consider the radius of sodium as the distance from a sodium nucleus to one of the fluorine valence pairs; should we take it equal to the radius of the sodium kernel; or should we assume it to be the distance between nearest atomic centers less the radius of the fluorine atom, calculated from other crystals, as does Bragg? In crystals of many of the metals a similar question arises. Perhaps it will be best not to use the term "atomic radius" at all in discussing such a crystal as this.[1]

[1] Since the above was written, an abstract of a paper by W. P. Davey has appeared, PHYS. REV. (2), *18*, 102 (1921), in which "radii" of alkali and halide *ions* are calculated on the assumptions (1) that the distance between atomic centers equals the sum of the radii, and (2) that the radii of K^+, Rb^+ and Cs^+ are equal respectively to those of Cl^-, Br^- and I^-.

The first assumption has just been shown to be invalid, but it is easy to see that, if the distance from nucleus to the outermost shell of an ion of a given element in different crystals is practically constant, the interatomic distances, *although not equalling the sum of the ionic radii*, will be approximately additive. (The actual values calculated have very little significance.)

The second assumption is probably nearly correct, for, the atomic radius of a *complete* atomic shell decreases but slowly as the nuclear charge is increased (considering the elements at the end of a period of the periodic system, *e.g.*, C, N, O, F, Ne, Na). However, the checks obtained by Davey from the interatomic distances of different crystals do not necessarily substantiate this assumption any more than they do the first, for if the "radius" of each negative ion were a certain distance *greater* than that assumed, and that of each positive ion were the same distance *less* than that assumed, the distance between centers of positive and negative ions would in each case be the same as that already computed.

It may similarly be said of Bragg's atomic radii calculations, that if his value for the radius of sulfur should prove to be too high, then practically all of the radii calculated directly or indirectly from this value for electronegative elements are too high and those calculated for electropositive elements are too low.

In this connection it is interesting to note a paper by R. N. Pease (J. Am. Chem. Soc., *43*, 991 (1921) and Chem. News, *123*, 121 (1921)) largely "devoted to establishing the fundamental correctness of the assumption that the outer shells of electrons in isosteres [atoms or groups of atoms having the same number and arrangements of electrons outside of the nuclei, but differing in the nuclear charges] have the same dimensions independent of the charges on the positive nuclei of the atoms or at least that the volume of the molecule as a whole shall behave as if this were the case." The approximate equivalence of the molecular volumes calculated for isosteres is merely the result of the fact that, except for hydrogen, the only atoms in the compounds compared are those of electronegative elements and the rare gases,—those near the ends of the periods of the periodic system, the very elements in which, as we have just stated, the atomic radius varies but slightly (but surely varies) with the atomic number (or nuclear charge).

In calcite, $CaCO_3$, each calcium atom is surrounded by six equidistant, symmetrically arranged oxygen atoms, each carbon atom by three equidistant oxygen atoms at the corners of an equilateral triangle and each oxygen atom by two similarly placed calcium atoms and one carbon atom. Each calcium supplies to the structure two valence electrons, each carbon four, and each oxygen six, a total of 24 for each $CaCO_3$ unit. Assuming the pair as the unit, as in diamond and sphalerite, there can be but one pair to each of the six identical calcium-oxygen bonds. There remain then 12 electrons to be distributed between three exactly equivalent carbon-oxygen bonds. There are four ways to do this in accord with the symmetry of the structure. Each carbon might be surrounded by six pairs *in one plane*, as in Figs. 2*A* and 2*B*; or each

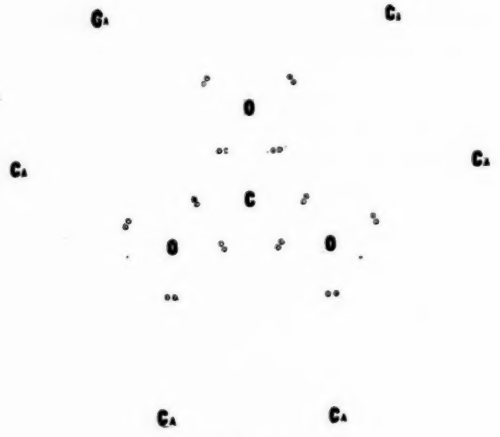

Fig. 2*A*.

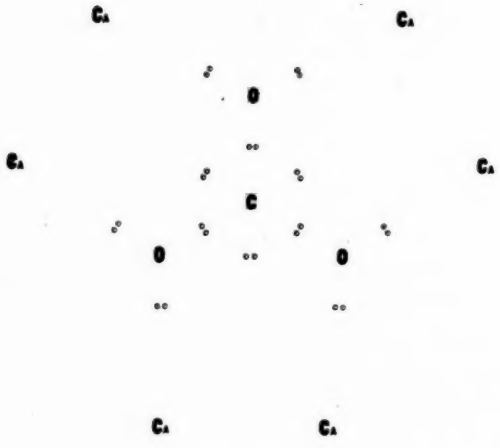

Fig. 2*B*.

carbon might be surrounded by but three pairs and each oxygen by four pairs, these last being *all in the same plane.*

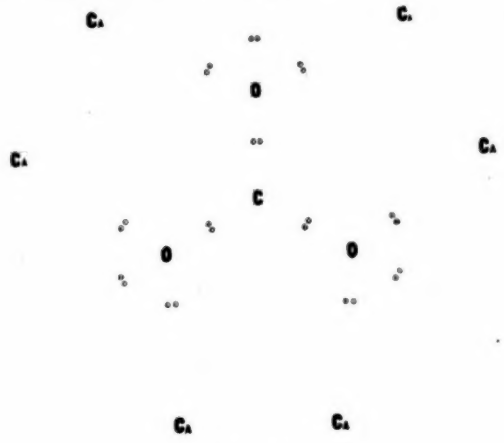

Fig. 2C.

Possible (but improbable) electron arrangements in calcite.[1]

By far the most probable arrangement, and the only one in which the arrangement of electrons around each oxygen atom is what we know it to be in other crystals, is that shown in Fig. 3. Each carbon is con-

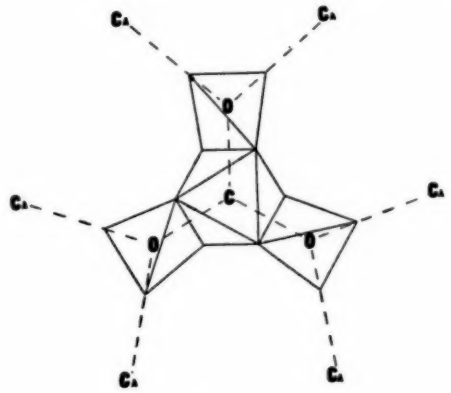

Fig. 3.

nected to the surrounding oxygens by double bonds. An octahedron of pairs is thus formed around each calcium and each carbon atom, and a tetrahedron of pairs around each oxygen atom.

If we assume this to be the correct structure, it is evident that the atomic spheres of the carbon and oxygen atoms interpenetrate, and their

[1] The calcium atoms in Figs. 2 and 3 are not in the plane of the paper, but are alternately above and below it.

radii, therefore, do not add up to give the distance between atomic centers.[1]

Causes of Variation of the Atomic Radius of an Element.—Let us now consider briefly the chief factors affecting the distance between atomic center and valence electronpair—the atomic radius—for a given element.

In the first place, in many crystals some of the valence pairs do not act as bonds. These are surely at a different distance from the nucleus—probably a smaller distance—than pairs which are bonds. In a crystal of quartz (SiO_2),[2] for example, each oxygen atom has a valence shell of four electronpairs, only two of which serve as bonds.

Second, for one reason or another, a valence electronpair may be forced away from its normal position in the valence shell.[3] This we might expect to result in an increased distance between nucleus and valence pair. Thus in the quartz crystal the angle subtended at the atomic center by the two bond electronpairs around each oxygen atom is considerably greater than it would be (about 109°) if the pairs were in their normal positions at the corners of a regular tetrahedron. Another good example of this is found in the marcasite (FeS_2) crystal. The distortions of the atoms in this substance have been discussed quite fully by the writer elsewhere.[4]

Third, widely varying pulls are exerted on electronpairs by atoms of different elements, hence the atomic radius depends to a considerable extent on the kind of atom to which the atom in question is bonded. We should not expect the radius of the oxygen atom to be exactly the same in the compounds ZnO, FeO, Cu_2O, and SiO_2. In the ammonium chloride crystal[5] (Fig. 4) the distance of each hydrogen nucleus from the valence pair connecting it to the nitrogen atom is surely different from that bonding it to the chlorine atom, hence, using the term in the sense in which it has been employed in this paper, the radius of the hydrogen atom in this crystal has two different values.[6]

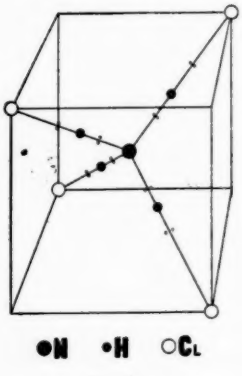

Fig. 4.

[1] This calcite structure practically proves that the double bond is what it has long been thought to be; at the same time it disproves the old idea that the carbon atom is *always* tetrahedral in shape.

[2] Huggins, PHYS. REV. (2), xix., p. 363 (1922).

[3] The author has shown that, in general, except for elements in the first row of the periodic table, valence pairs *tend* to place themselves opposite the centers of the faces of the next underlying atomic shell of electrongroups (*i.e.*, on lines passing through the center of the atom and the center of each face of the outermost kernel shell).

[4] PHYS. REV. (2), xix., p. 369 (1922).

Fourth, an atom of the same element in different structures may pull an electronpair away a different distance from the nucleus of the atom to which it is bonded. An example of this is found in the two forms of zinc sulfide—sphalerite and wurzite—which differ only in the way the layers of atoms are placed over one another. The distance between planes of zinc and sulfur atoms is found to be slightly greater in wurzite than in sphalerite.

Fifth, if an atom has a different number of electronpairs in its valence shell in two crystals, we should not expect their distances from the nucleus to be the same in the two cases. Thus, each carbon atom is surrounded by four pairs in diamond and by six in calcite.

Sixth, valence electronpairs are pulled out from the nucleus to a different extent according to whether they are on the centerlines or not. This may have some effect on the oxygen radius in quartz, for it is probable that the electronpairs bonding each oxygen to silicon atoms are not on the Si−O centerlines. Whenever this is the case, the radius computed by Bragg's method will not be the true radius.

Seventh, many atoms are capable of more than one arrangement of electrons in that part of the atom inside of the valence shell, which Lewis has designated the "kernel." This manifests itself in a variability of the number of valence electrons and of the atomic radius. An extreme example of this is probably furnished by the element manganese (for which Bragg gives two values of atomic radius, 1.17 Å. and 1.47 Å.).

Eighth, in some crystals, notably in graphite[1] the electronic structure of which is to be described in a forthcoming paper, and in many organic compounds, the number of electrons constituting a bond is more than two. Wherever this is the case, the distances from the atomic nuclei to these electrongroups (and also to electronpairs in the same crystal) are quite different from the atomic radii of the same atoms in other crystals. In diamond the atomic radius of carbon is 0.77 Å.; in graphite each atomic center is surrounded by three electronsextets and one electronpair, the distance to each being about 1.45 Å.

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[5] Bragg and Bragg, loc. cit., p. 158; Bartlett and Langmuir, J. Am. Chem. Soc., *43*, 84 (1921); Huggins, "Electronic Structures of Crystals II," soon to be published.

[6] In this case we might properly speak of the "diameter" of the hydrogen atom, meaning the distance through the atomic nucleus from electronpair to electronpair; but in considering atoms in which there are not two valence pairs on diametrically opposite sides of the nucleus (which is the case for most atoms in most crystals), the term "atomic diameter" has no physical meaning.

THE CRYSTAL STRUCTURES OF ARAGONITE ($CaCO_3$) AND RELATED MINERALS.

By Maurice L. Huggins.[1]

Synopsis.

The Structure of Aragonite.—A structure is proposed for aragonite which is in accord with all observed facts. As in calcite, each carbon atom is bonded (by double bonds) to three oxygen atoms, each oxygen to two calciums and one carbon, and each calcium to six oxygens, at the corners of an irregular octahedron. The distortions of the structure are considerable; their magnitudes and causes are discussed.

Cleavage Planes.—The observed cleavage of aragonite is shown to be in accord with the following principles:—(1) Cleavage tends to occur so as to leave the two new crystal surfaces electrically neutral. (2) Where some bonds are weaker than others, cleavage will take place in such a way as to rupture the weaker bonds in preference to the stronger ones. (3) All bonds being equally strong, cleavage will occur between the planes connected by the fewest bonds per unit area.

The Structures of $SrCO_3$, $BaCO_3$ and $PbCO_3$.—The dimensions and interatomic distances in the isomorphous minerals strontianite, witherite and cerussite, which are assumed to have similar structures, are computed.

Electron Arrangements in Accord with the Author's Theory.—These structures are shown to be in conformity with the author's theory that the electrongroups in an atomic shell tend to place themselves opposite the faces of the imaginary polyhedron formed by the electrongroups in the next underlying shell.

ALTHOUGH the structure of calcite has been known for several years,[2] the arrangement of the atoms in aragonite, the orthorhombic form of $CaCO_3$, has not heretofore been published.

The arrangement of the electrons in calcite has been obtained, with the aid of the Lewis theory of atomic and molecular structure,[3] by the author.[4] We might expect the electronic and atomic arrangement about each atom to be very similar in the two crystals. By provisionally assuming this, the author has been able to work out the aragonite structure.

The Arrangement of Carbon and Calcium Centers.—The arrangement of the centers of carbon and calcium atoms is illustrated in Figs. 1, 2 and 3. Carbon atoms are represented by dots, calcium atoms by circles. The lines in Figs. 1 and 3 indicate which C and Ca atoms are bonded together

[1] Dupont Fellow in Chemistry, University of California, 1921–22.

[2] W. L. Bragg, Proc. Roy. Soc., *A89*, 468 (1914), Bragg and Bragg, X-rays and Crystal Structure, G. Bell and Sons, 1919, p. 112. Wyckoff, Am. Jl. Sci. (4), *50*, 317 (1920).

[3] G. N. Lewis, J. Am. Chem. Soc., *38*, 762 (1916).

[4] Huggins, Phys. Rev. (2) xix, p. 346, 1922.

(through oxygen atoms) although they do not show the actual positions of the bonds. Fig. 1 shows the arrangement in each 001 (basal) plane. These planes are laid over one another in such a way as to produce a face-centered lattice, the unit of which is shown in Fig. 2. Fig. 3 gives

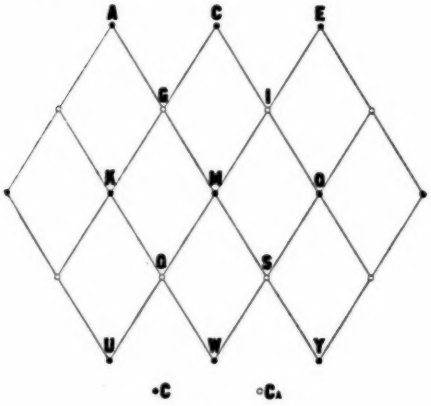

Fig. 1.
Arrangement of C and Ca atoms in each 001 plane.

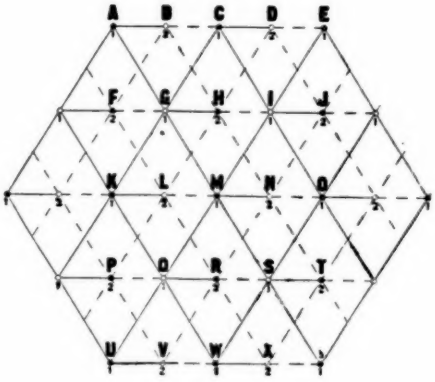

Fig. 3.
Plan C and Ca atoms only.

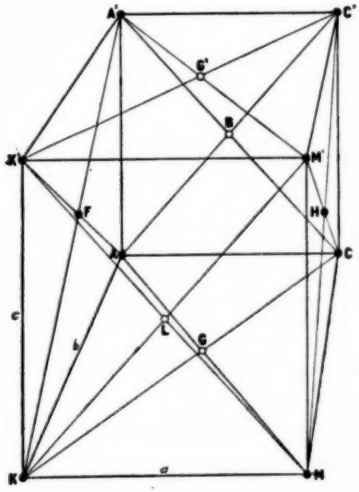

Fig. 2.
Unit cell. C and Ca atoms only.

the structure in plan. The atoms are numbered to indicate in which plane each atomic center lies. Lines between atoms in planes 1 and 1 or 1 and 2 are shown full; those between atoms in planes 2 and 2 or 2 and 1′ (the next plane above 2) are dotted. The lettering in each of these diagrams corresponds to that in the others.

The Arrangement of Oxygen Atoms and Valence Electrons.—Fig. 4 shows the arrangement of calcium and oxygen atoms around each carbon atom in calcite. The central octahedron, H, is a carbon atom, the sur-

rounding tetrahedra are oxygen atoms, and the letters D, B, G, L, N, and I′ show the relative positions of the calcium atoms. Each oxygen is surrounded by four pairs of electrons, at the tetrahedron corners, two

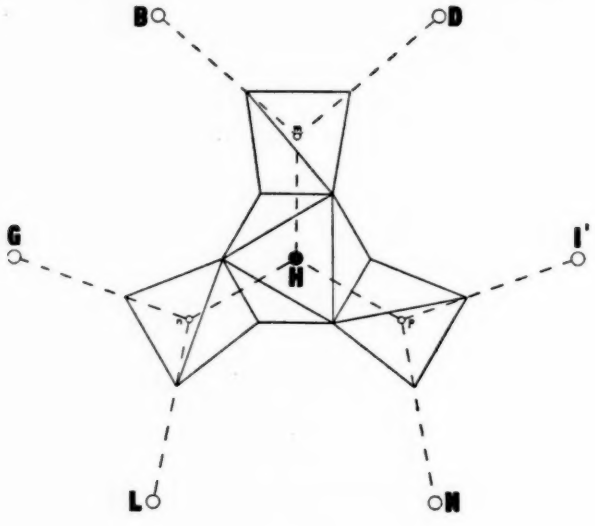

Fig. 4.

Arrangement around a carbon atom (H), in both calcite and aragonite.

of which serve as bonds connecting it to the adjacent calcium atoms, and two forming a double bond joining it to the carbon atom (H). This gives six pairs of electrons, at octahedron corners, around each carbon atom. Each calcium atom is also surrounded by six electronpairs at octahedron corners.

This same arrangement exists in aragonite, although it is distorted to some extent. The carbon atom H, for instance, is bonded, through oxygen atoms, to calcium atoms D, B, G, L, N, and I′, as shown in Fig. 5. (In this figure and in Fig. 6 the lines represent bonds between atoms.) The positions of the oxygen atoms and of the valence electronpairs, relative to the other atoms, is thus approximately determined, for we may assume the distance from carbon center to oxygen center to be practically the same as in calcite (1.28 Å.[1] = 1.28×10^{-8} cm.).

The Dimensions of the Lattice, and Distances between Atoms.—We shall now calculate the actual dimensions of the structure. Groth [2] gives the density of aragonite as 2.926 — 2.933 g./c.c. and the axial ratio as $a : b : c = 0.6228 : 1 : 0.7204$ (= KM : KA : KK′, Fig. 2).

[1] W. L. Bragg, Nature *106*, 725 (1921).

[2] Chemische Krystallographie, Vol. II., p. 206.

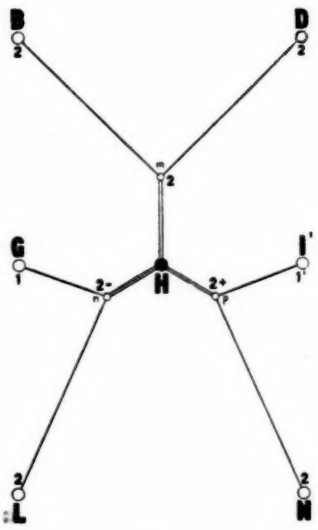

Fig. 5.

Arrangement around a carbon atom (H).

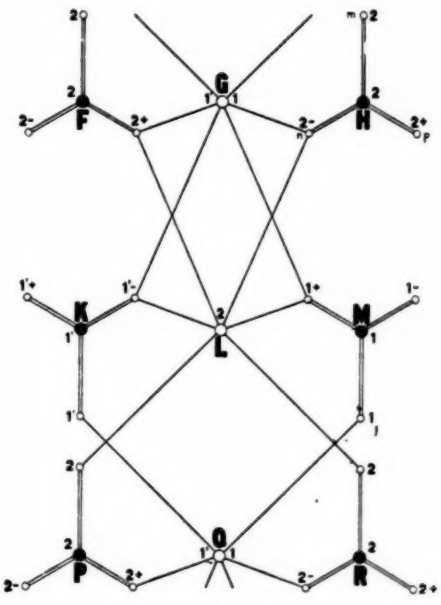

Fig. 6.

Arrangement around a calcium atom (L).

The volume of the unit cell is equal to

$$\frac{\text{no. molecules per cell} \times \text{molec. wt.}}{\text{no. molecules per mol} \times \text{density}} = \frac{2 \times 100.075}{0.6062 \times 10^{24} \times 2.9295} \text{ cm.}^3$$

$$= 112.7 \times 10^{-24} \text{ cm.}^3$$

Then

$$b = \text{KA} = \sqrt[3]{\frac{112.7 \times 10^{-24} \text{ cm.}^3}{0.6228 \times 0.7204}} = 6.310 \times 10^{-8} \text{ cm.} = 6.310 \text{ Å.}$$

From this

$$a = \text{KM} = 0.6228 \times 6.310 \text{ Å.} = 3.930 \text{ Å.}$$

and

$$c = \text{KK}' = 0.7204 \times 6.310 \text{ Å.} = 4.546 \text{ Å.}$$

The calcium-carbon distance in calcite (HB = HD = HI, etc., Fig 4) is given by W. L. Bragg [1] as 3.206 Å. The corresponding distances in aragonite, calculated from the unit distances given above, are

$$\text{HB} = \text{HD} = \text{HN} = \text{HL} = 3.717 \text{ Å}, \qquad \text{HI}' = \text{HG} = 3.004 \text{ Å}.$$

The calcium-carbon-calcium angle in calcite ($\angle$BHD = $\angle$I'HN, Fig. 4) is 78° 05′. In aragonite $\angle$BHD = 63° 50′ and $\angle$I'HN = 69° 46′.

[1] Nature *106*, 725 (1921).

It is evident from the above comparison, that although the general arrangement of atoms is the same and the distances in the two crystals between corresponding atoms are approximately the same, there is considerable distortion (chiefly in the *b* direction) of the structure in aragonite from the more symmetrical marshalling of calcite. This may largely be accounted for in the following way:

Let us assume, for this purpose, that the distance between nearest calcium and carbon centers (HI′, HD, HN, etc.) *tends* to be 3.206 Å. and that the Ca−C−Ca angle (∠BHD, ∠I′HN, etc.) tends to become 78° 05′. Now if *a* and *c* had the values calculated for them, and if ∠I′HN were 78° 05′, the distance HN and the angle LHN (= ∠BHD) would have to be 6.22 Å. and 36° 48′, respectively. On the other hand, if *a* and *c* were as calculated, and HN were 3.206 Å., then angles LHN and I′HN would be 75° 34′ and 66° 23′, respectively.

It is apparent that with the kind of structure assumed it would be impossible for the Ca−C distances HI′ and HN to both be the same as in calcite, if ∠I′HN were 78° 05′ (as in calcite); and vice versa. The actual structure is a compromise between these two extremes (for which calculations were made in the preceding paragraph). ∠I′HN is 69° 46′, intermediate between 66° 23′ and 78° 05′, and HN is 3.717 Å., intermediate between 3.206 Å. and 6.22 Å. ∠LHN, 63° 50′, is also midway between the extremes 36° 48′ and 75° 34′.

HI′ in aragonite (Fig. 5) is slightly less than the corresponding distance HI′ in calcite (Fig. 4). This may be attributed to the tendency of a valence electronpair to be drawn closer to the nucleus (of oxygen, in this case) if another pair (or other pairs) in the same valence shell is pulled out away from the nucleus by any cause.[1]

We have here an excellent example of the variability of the distance between the nucleus and a valence electronpair (the atomic radius) for a given element. If the distance from nucleus to one electronpair is about 24 per cent. greater than that to another *in the valence shell of the same atom*, then we must be very careful about assuming these distances (the atomic radii) to be the same for a given element in different crystals, which have entirely different structures. The variation in radius is, in general, very much less for electro-negative elements than for electro-positive elements, the alkali and alkaline earth elements showing the greatest variation.[2]

Cleavage Planes.—Cleavage planes in a crystal, the author assumes to be determined, in general, by the following considerations:

[1] Cf. Lewis, loc. cit.; Latimer and Rodebush, J. Am. Chem. Soc., *42*, 1419 (1920); and Huggins, idem., "Electronic Structures of Some Organic Compounds," soon to be published.

[2] Huggins, PHYS. REV. (2) **xix**, p. 346, 1922.

1. Cleavage tends to occur so as to leave the two new crystal surfaces electrically neutral.

2. Where some of the bonds in a crystal are weaker than others,[1] cleavage will take place in such a way as to rupture the weaker bonds in preference to the stronger ones.

3. All bonds being equally strong, cleavage will occur between the planes connected by the fewest bonds per unit area (of the cleavage plane).

Without considering here the justification for the above assumptions, it will be pointed out that they are in full accord with the aragonite structure which has been described, and the observed cleavage planes of aragonite crystals.

According to Groth[2] the most marked cleavage is between the 010 planes, imperfect cleavage occurring parallel to the 110 and 011 planes, but none between 001 or 100 planes.

Now we may be sure, from chemical considerations, because oxygen and carbon atoms hold onto electrons more tightly than do calcium atoms, that whenever a rupture occurs, it will be between a calcium kernel and the valence pair by which it is bonded to an oxygen kernel. This will leave an excess positive charge on the calcium and an excess negative charge on the oxygen, or, perhaps we should say, on the carbonate group. So, according to the first condition given above, cleavage must be in such a way as to leave an equal number of these positive calcium atoms, and also of the negative carbonate groups, on each side of the break, it being impossible for the cleavage plane to separate a plane containing only calcium atoms from one containing only carbonate groups. This at once eliminates the 100 and 001 planes, as may be seen from Fig. 3.

Since the distances (HB, HD, HN, etc., Fig. 5) between calcium and carbon atoms in the same 001 plane are much greater than those (HG, HI′) between carbon and calcium atoms in different 001 planes, we may feel sure that the Ca−O distances Bm, Dm, Ln, Np, etc., are greater than the distances Gn, I′p, etc. It seems reasonable to assume, then, that the former Ca−O bonds are weaker than the latter. In accordance with this and with condition 2 above, is the marked cleavage between 010 planes, this being the only way in which it may occur without causing the rupture of any of the bonds of the Gn, I′p type. Cleavage in the 110 and 011 directions ruptures fewer bonds (either considering all the Ca−O

[1] By the strength of a bond is here meant the force resisting breakage in the direction normal to the cleavage plane being considered. Hence a bond normal to the cleavage plane must be considered to have a greater "strength"—for this purpose—than a similar bond not normal to the plane of cleavage.

[2] Loc. cit.

bonds or only those of the stronger type) per unit area than that in any other direction (except those already considered). Here also the observed result is in accord with the principles outlined above.

Comparison with $BaCO_3$, $SrCO_3$ and $PbCO_3$.—Isomorphous with aragonite are the minerals strontianite ($SrCO_3$), witherite ($BaCO_3$) and cerussite ($PbCO_3$).[1] From the densities, axial ratios and molecular weights, the dimensions of the unit cell have been computed for each of these, exactly as was done for aragonite; also the angle BHD and the distances (Fig. 5) BH, HN and Bm (the metal-oxygen distance, calculated on the assumption that Hm, the carbon-oxygen distance, is 1.30 Å. in each crystal).[1] These are given in Table I., alongside of the aragonite values.

TABLE I.[2]

	Aragonite $CaCO_3$.	Strontianite $SrCO_3$.	Witherite $BaCO_3$.	Cerussite $PbCO_3$.
Density (g./c.c.)....	2.926–2.933	3.680–3.716	4.28–4.37	6.574
Vol. of unit cell = 2 × molec. volume.	112.7 Å.^{3}	131.7 Å.^{3}	150.6 Å.^{3}	134.1 Å.^{3}
Axial ratio $a : b : c$.	0.6228 : 1 : 0.7204	0.6090 : 1 : 0.7237	0.5949 : 1 : 0.7413	0.6102 : 1 : 0.7232
a (KM).....	3.930 Å.	4.072 Å.	4.158 Å.	4.102 Å.
b (KA).....	6.310 Å.	6.686 Å.	6.989 Å.	6.723 Å.
c (KK').....	4.546 Å.	4.838 Å.	5.181 Å.	4.862 Å.
HB.....	3.717 Å.	3.914 Å.	4.066 Å.	3.938 Å.
HI'.....	3.004 Å.	3.162 Å.	3.322 Å.	3.181 Å.
Bm.....	2.70 Å.	2.88 Å.	3.02 Å.	2.91 Å.
∠BHD.....	63° 50′	62° 40′	61° 30′	62° 47′

Atomic Theory.—In a previous paper the writer has presented a system of atomic structures (practically identical with the Lewis theory for the lighter elements), which is based largely on the idea that the electrongroups (pairs or triplets) in an atomic shell tend to occupy positions opposite the centers of the faces of the imaginary polyhedron formed by the electrongroups in the next underlying shell.[4] Thus, if the underlying shell consists of eight electrongroups arranged at cube corners, the next shell further out will consist of six groups, at the corners of an

[1] Bromlite, (Ba, Ca)$(CO_3)_2$, and manganocalcite, RCO_3, in which R represents Mn, Mg, Ca, and a little Fe, might also be included, but their compositions, and hence their densities and axial ratios, are variable.

[2] The densities and axial ratios are obtained from Groth. loc. cit.; in each case the mean of the values given for the density was used in the computations.

[3] The average of the values 1.28 Å. and 1.30 Å. given for this distance in calcite and rhodochrosite ($MnCO_3$), respectively, by W. L. Bragg, Nature *106*, 725 (1921).

[4] The arrangements of electrons in atoms of elements in the first row of the periodic table are governed by other considerations.

imaginary octahedron, each of which is opposite a face of the underlying cube. This idea is of great importance in the determination and discussion of crystal structures, for the number of valence electrons and the relative positions which they tend to occupy are the chief factors which determine the arrangement of the atoms in a crystal of a given substance.

It has been shown in other papers that, in a great many cases at least,[2] the arrangement of valence pairs in crystals is in accordance with the foregoing idea, each pair being oppositeaface of the next kernel shell underneath, in both atoms connected by the pair (if it is acting as a bond, and so is in two valence shells).

The crystals discussed in this paper are no exceptions to this rule. The outermost kernel shell, in a calcium, strontium, or barium atom, consists of a cube of pairs, and the structure we have assigned to these crystals indicates that there are six pairs around each metal atom, arranged at the corners of a somewhat distorted octahedron—that is, opposite the faces (but not the *centers* of the faces) of the kernel cube. Some of the causes of the distortions have already been discussed. The outermost shell in the kernel of a *divalent* lead atom, if the author's structure for it is correct, consists of six pairs at the corners of an octahedron. Now an octahedron has eight faces, but in the lead carbonate crystal only six of them are occupied by valence pairs (the two unoccupied faces being on diagonally opposite sides of the atom). These six are themselves at the corners of a distorted octahedron. As a matter of fact, since the angle between cube diagonals is 70° 32′, whereas that between diagonals of a regular octahedron is 90°, and the actual angle between bonds in these crystals is in the neighborhood of 62° or 63°, the displacement of the bonds from what we might call their normal positions—through the centers of the faces of the kernel polyhedra—is much less for lead than for calcium, strontium or barium. This is as we should expect, for lead is much less electropositive than the alkaline earths, and we have every reason to believe that its valence electrons are more closely

[1] Huggins, PHYS. REV. (2), xviii, p. 333, 1921, and PHYS. REV. (2), xix, p. 346, 1922.

[2] The orienting effect of the kernel upon the valence electrons is much less in the alkali and alkaline earth elements, where the valence electrons are not drawn close to the kernel, than in more electronegrative elements.

Most of the alkali halides, the alkaline earth oxides and sulfides, a few other binary compounds, and many of the metals possess a somewhat different type of structure, in which the atoms are held together by what may be called "distributed bonds," in which the valence pairs are not on the centerlines between nearest atoms, rather than "localized bonds" of the ordinary single or double bond type. In these crystals also, however, there is a manifest tendency for electronpairs *or groups of electronpairs* to be placed opposite the faces of the underlying atomic shells.

and more tightly held than those of the other metals under consideration. (The metal-oxygen distance Bm is practically the same for lead as for strontium, although the atomic numbers are 82 and 38, respectively.)

It is of interest in this connection that in crystals of smithsonite ($ZnCO_3$), magnesite ($MgCO_3$) and some other minerals isomorphous with calcite, the valence shell of the metal atom consists of six electronpairs, at octahedron corners, outside of a kernel shell of four pairs, at tetrahedron corners.[1] The state of affairs is here just the opposite of that in lead carbonate. Only half of the eight faces of the *valence* shell are occupied (*on the inside*) by *kernel* pairs. This arrangement is symmetrical, however, and seems to be possible where the valence pairs are drawn far enough away from the kernel by the attractions of other atoms.[2]

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[1] Many cases of a tetrahedron outside of an octahedron are known. Cf. the author's paper last referred to.

[2] Other examples of this phenomenon, existing outside of the crystalline state, are afforded by the compounds H_2SiF_6 and SF_6, in each of which there is a valence shell of six pairs outside of a kernel shell of four pairs.

THE CRYSTAL STRUCTURE OF QUARTZ.

BY MAURICE L. HUGGINS.[1]

SYNOPSIS.

The Structure of Quartz (SiO_2).—By means of the Lewis theory, a structure has been obtained for quartz which accounts in a satisfactory way for the crystalline form, crystal symmetry, optical rotation, hardness, high melting point, insolubility, and x-ray spectra of the substance. It is in strict accord with the conclusions of W. H. Bragg in regard to the structure. Furthermore, the distance between adjacent silicon and oxygen atoms, calculated from the dimensions of the lattice, as obtained by Bragg, is approximately equal to the sum of their atomic radii, obtained from other crystals.

The Arrangement of Atoms and Electrons.—Each silicon atom is surrounded by four pairs of electrons at tetrahedron corners, which act as bonds connecting it to four equidistant oxygen atoms. Each oxygen atom is also surrounded by four tetrahedrally oriented electronpairs, two of which serve as bonds connecting the oxygen to silicon atoms. *The crystal is thus not made up of SiO_2 units, but is a single molecule,* for all of the bonds around each silicon or each oxygen atom are of the same type—the usual type of bond which connects the atoms in a molecule.

QUARTZ crystals are placed by crystallographers in the trapezohedral class of the trigonal system, possessing three-fold symmetry about a vertical axis, but having neither plane of symmetry nor center of symmetry. They are enantiomorphic, being of two kinds, which are to each other as an object and its mirror image, and which rotate polarized light in opposite directions. The usual form of crystal is that of a hexagonal prism, terminated at each end by a pyramid, some of the corners, however, being modified by small faces of other types.

W. H. Bragg[2] has obtained x-ray reflections from several faces of a quartz crystal, his measurements being, in the main, such as would be

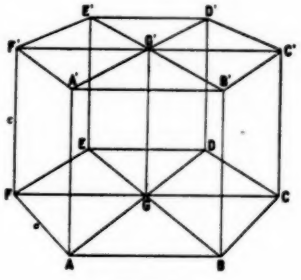


Fig. 1.

[1] Dupont Fellow in Chemistry, University of California, 1921–22.

[2] W. H. Bragg, Proc. Roy. Soc., *A89*, 575 (1914); Bragg and Bragg, X-Rays and Crystal Structure, G. Bell and Sons, London, 1918, page 160.

obtained if the scattering centers were at the points of a triangular prism lattice (Fig. 1) of dimensions, $a = 4.89$ Å. (1 Ångstrom unit $= 10^{-8}$ cm.) and $c = 5.375$ Å. However, the reflections from the basal planes were such as to indicate a distance between planes just one-third of c, or 1.792 Å. Also it was calculated, from the density of the crystal, that three molecules of SiO_2 are associated with each point of the lattice. Bragg therefore reasoned that the structure is based on three interpenetrating lattices of the type shown, these being "so related that they can be derived from each other by a rotation of $2\pi/3$ about, and a translation $c/3$ along, an axis parallel to the c direction. Thus each trigonal axis of the structure has points arranged spirally around it, and since a spiral may be either right- or left-handed, we can understand the reason for the two forms of quartz."

This was as far as Bragg could go. He was not able to determine either the amount of the relative displacement of the interpenetrating lattices or the disposition of the atoms around the points of these lattices. It has been found possible, however, by means of the Lewis theory of valence and atomic structure,[1] which the author has successfully applied [2] to the structure of a large number of crystals, to obtain a complete solution of the structure, which is in entire accord with Bragg's conclusions.

According to the Lewis theory, there are sixteen valence electrons per SiO_2 group—six per oxygen atom and four per silicon atom. Each oxygen and each silicon atom tends to surround itself by four pairs of electrons, arranged at the corners of a tetrahedron. These pairs may act as bonds, in which case they each form a part of the valence shells of two atoms, or they may be "lone pairs"—pairs not acting as bonds between atoms. It seems highly probable, moreover, from a consideration of analogous substances, that in the quartz crystal the bonds are all Si—O bonds.

If the above assumptions are correct—sixteen electrons per SiO_2 unit, a tetrahedron of pairs around each atom, and Si—O bonds only—then each silicon must be bonded to four oxygen atoms, arranged at the corners of a tetrahedron, and each oxygen atom must be bonded to two silicon atoms, which are also at two of the corners of a tetrahedron. (We should not expect this tetrahedron to be regular, for two of the electron pairs around each oxygen atom are lone pairs and two are bond pairs. The magnitude of this distortion and the effect on the structure will be discussed later in this paper.)

The Quartz Structure.—With the aid of the foregoing ideas the author has obtained the structure for quartz represented in plan in Fig. 2. In

[1] Lewis, J. Am. Chem. Soc., *38*, 762 (1916).

[2] Huggins, idem.

this figure there are shown three consecutive layers of atoms, each of which is normal to the trigonal axis. The atoms are numbered 1, 2 or 3, according to whether they are in the first, second or third layer from the bottom. The fourth layer is identical with the first, the fifth with the second, etc.; (3) means the layer, identical with 3, next below layer 1. The solid dots represent the centers of silicon atoms and the circles the centers of oxygen atoms. The double circle indicates that there are two oxygen atoms, in different layers, one over the other.[1] The bonds connecting the atoms are represented by full lines. These are of two lengths (in the diagram); the longer lines connecting atoms in the same layer; the shorter lines connecting atoms in different layers. (The actual distances between atomic centers are of course the same, or very nearly the same, in the two cases.) Each of these shorter lines is doubled, to represent, not a "double bond," but two single bonds, connecting a silicon in layer 2, for instance, with oxygens in layers 1 and 3, or a silicon in layer 1 with oxygens in layers (3) (below) and 2 (above).

Each silicon kernel is surrounded by four pairs of valence electrons, bonding it to four equidistant, tetrahedrally oriented, oxygen atoms, and each oxygen kernel by four tetrahedrally arranged electron pairs, two of which serve as bonds connecting the oxygen to two silicon atoms, the other two being lone pairs.

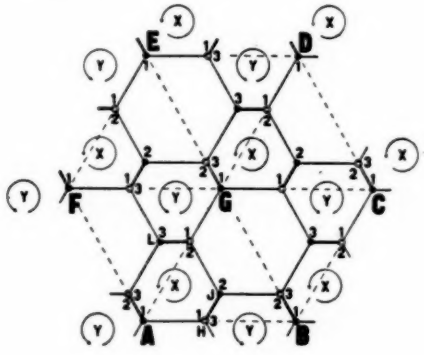


Fig. 2.

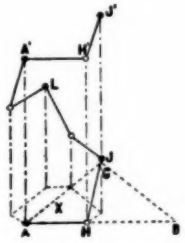


Fig. 3.

X and Y denote axes around each of which there is a spiral of silicon and oxygen atoms. One of these spirals is shown in Fig. 3. It may be readily seen from Fig. 2 that equivalent, similarly situated points in the structure (such as points X, or points A, B, C, D, E, F and G, the lettering in Figs. 1 and 2 corresponding) are at the points of a lattice of the type shown in Fig. 1. For each point of the lattice there are three silicon

[1] This is not strictly true because of their distortions. See the later discussion on this subject.

and six oxygen atoms, arranged spirally in three similar layers, the vertical distance between layers being just one third the height of the unit prism. Thus the x-ray spectra, the crystalline form, the existence of right- and left-handed crystals, and the optical rotation of the substance are all accounted for.

Distortions from the Structure Described.—Let us now consider the distortion from the structure shown in Figs. 2 and 3. Of the four electron pairs surrounding each oxygen kernel only two are acting as bonds, hence their arrangement cannot be that of a *regular* tetrahedron. It seems reasonable to suppose that the bond pairs are further from the atomic center than the lone pairs, and that the angle formed by the imaginary lines connecting the atomic center with the bond pairs is somewhat greater than 109° 28′, its value if the electron pairs were at the corners of a regular tetrahedron.

Since we do not know this angle, it is impossible either to compare this structure quantitatively with the known dimensions of the lattice, as determined by Bragg, or to calculate directly the exact position of the atoms relative to each other. But by assuming this structure to be correct, and taking the distance between adjacent silicon and oxygen atomic centers as equal to the sum of their atomic radii, obtained from other crystals, the angle between silicon-oxygen bonds can be calculated from the lattice dimensions. If it proves to be some value somewhat greater than 109° and considerably less than 180°, then this constitutes a rough check on the structure. Or, we may do what amounts to the same thing—we may calculate the Si−O distance on the assumption that the angle between bonds is 109° 28′; and this distance, if our reasoning is correct, should be a few per cent. greater than the distance calculated from the atomic radii. We shall see that this is the case.

If the angle between the two bonds connecting each oxygen to silicon atoms ($\angle AHJ$, Fig. 4) were 109° 28′, the distance between adjacent silicon and oxygen atom centers ($AH = HJ$), computed from the dimensions of the lattice, would be 1.97 Å. Now the radius of the silicon atom—the distance from atomic center to valence electron-pair—in a crystal of the element[1] is 1.17 Å. Bragg[2] computes the radius of the oxygen atom, from dimensions of the ZnSp, ZnS, and FeS_2 structures, to be 0.65 Å. Transferring these values of atomic radii to the quartz crystal, we get 1.82 Å. as the approximate distance between silicon and oxygen atomic centers.[3]

Fig. 4.

[1] Debye and Scherrer, Phys. Zeit., *17*, 277 (1916); Hull, PHYS. REV., (2) ix, 566, 1917; Gerlach, Physik. Zeitsch., xxii 557. 1921.

[2] Phil. Mag., *40*, 169 (1920).

Each oxygen atom in the crystal is then displaced from the position H (Fig. 4) to a position K, about 1.82 Å. from the nearest silicon atoms. If we make the assumption that K is in the same plane as A, H and J, then the angle AKJ between the oxygen-silicon bonds can be calculated to be about 125°.

We are now in a position to calculate the relative positions of the silicon atoms (*e.g.*, of J, Figs. 2 and 3, relative to AB). The calculations are but a matter of geometry and simple trigonometry, but the results based on the Si−O distance 1.82 Å. and the angle $AKJ = 125°$, are of interest (although they must only be considered approximate). The projection of the silicon atom J on plane 1 is on the perpendicular bisector of the line AB, at a distance of 0.73 Å. from AB. Similarly, the projection of L is on the perpendicular bisector of AG, and 0.73 Å. from it, etc.

Discussion.—This structure agrees with the Lewis theory in every particular—in the number of valence electrons, in their tetrahedral arrangement around the silicon and oxygen atoms, and in the fact that each bond is in reality a pair of electrons in the shells of two atoms at the same time. It should be noted further that the Si−O bonds are single rather than double bonds[1] (as would be expected from the formula O = Si = O), this being in accordance with a generalization made by Lewis, and accounted for on theoretical grounds by the author,[2] that the elements which form double bonds readily (*e.g.*, carbon, nitrogen, oxygen) are all in the first row of the periodic table. The silicon and oxygen atoms do not occur in SiO_2 units, it being impossible to tell with what oxygen atoms a given silicon atom was "originally" bonded (before crystallization). Every atom in the crystal is connected to every other atom through bonds which are all of the usual type connecting atoms in a molecule; hence the whole crystal is a single molecule.

We might represent an isolated SiO_2 molecule in this way

$$\begin{matrix} \cdot\cdot & & \cdot\cdot \\ :\mathrm{O}: & \mathrm{Si} & :\mathrm{O}: \\ \cdot\cdot & & \cdot\cdot \end{matrix}$$

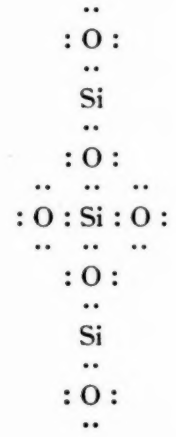
the electronpairs around both the oxygen and silicon atoms being understood to be at tetrahedron corners. Now the tendency of the silicon

[1] A double bond being a bond in which *two* pairs of electrons hold together two atoms.

[2] J. Am. Chem. Soc., "Electronic Structures of Atoms," soon to be published.

[3] This must be considered only an approximation, for the distance from atomic center to bond electronpair is surely different in a crystal in which all four valence pairs are acting as bonds (ZnO) from that in a crystal in which only two of them are bonds (SiO_2). Also, the bond pairs in quartz may not be quite on the centerlines between atoms, but slight displacements such as might be expected would have a negligible effect on the interatomic distances. Considering everything, the value 1.82 Å. is probably too small.

atom to surround itself by *four* electronpairs is very great, and it does this by attracting the oxygen atoms from two more molecules, giving the structure



The new silicon atoms attract more oxygens, and this process is continued indefinitely, the tetrahedral arrangement of the bonds producing the structure of quartz.

Crystal formation in this case, then, as in the case of most minerals, consists chiefly of a reaction between an atom (O) containing a lone electronpair in its valence shell and another atom (Si) capable of holding on to that lone pair, the result being a stable single bond. The stability of these bonds, in the case of quartz, is evidenced by its hardness, high melting point, insolubility, etc., which would be difficult to account for if the crystal were composed of saturated molecules held together by secondary valence.

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THE CRYSTAL STRUCTURES OF MARCASITE (FeS_2), ARSENOPYRITE (FeAsS) AND LOELLINGITE ($FeAs_2$).

By Maurice L. Huggins.[1]

Synopsis.

The Structure of Marcasite.—An arrangement of atoms and valence electrons, which is consistent with all known experimental facts, is proposed for marcasite (FeS_2). The arrangement around each atom is very similar to that in pyrite. The sulfur atoms are in pairs. Each sulfur is bonded, by pairs of electrons, to one sulfur and four iron atoms, and each iron atom to six sulfur atoms. Taking the unit distance from the dimensions of the pyrite structure, the density is computed, the value obtained being the same as that experimentally observed, within the limits of experimental error. The distortions of the atoms in the structure are discussed.

The Structures of Arsenopyrite (FeAsS) and Loellingite ($FeAs_2$).—Assuming the same general arrangement for arsenopyrite and loellingite as for marcasite, the dimensions of the unit cells are obtained, and these compared with those of marcasite.

Pyrite.—FeS_2 crystallizes in two forms, one (pyrite) being cubic, the other (marcasite) orthorhombic. By means of x-rays W. L. Bragg[2] has determined the structure of pyrite. He finds (Fig. 1*A*) that the

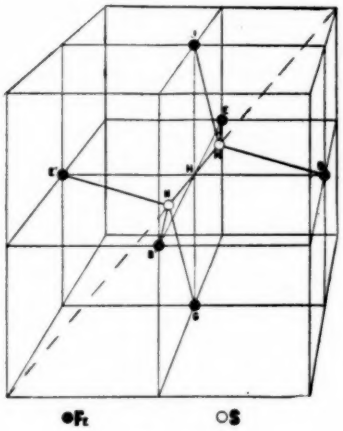

Fig. 1 *A*.

Illustrating the arrangement around each S–S group in pyrite.

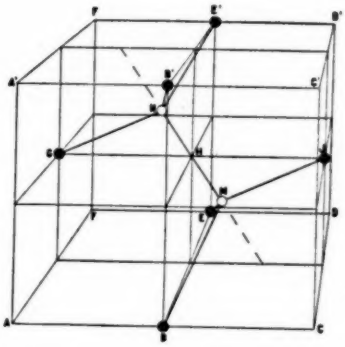

Fig. 1 *B*.

Illustrating the arrangement around each S–S group in marcasite.

sulfur atoms occur in pairs, each sulfur being surrounded by one sulfur and three iron atoms, at the corners of an imaginary tetrahedron. Each

[1] Dupont Fellow in Chemistry, Univ. of California, 1921–22.

[2] W. L. Bragg, Proc. Roy. Soc., *A89*, 468 (1913); Bragg and Bragg, X-rays and Crystal Structure, G. Bell & Sons, 1918, p. 127.

iron atom is surrounded by six sulfur atoms, at octahedron corners. As the author has previously pointed out,[1] if each iron furnishes two valence electrons to the structure, and each sulfur six, then there are fourteen electrons per FeS_2, just the number required for a pair of electrons on (or near) the centerlines between two adjacent atoms—each pair being in the valence shells of two atoms at the same time. This is in strict accord with the Lewis theory of the structure of atoms and molecules[2] and the author's extension of that theory.[3]

Marcasite.—Assuming that the arrangement of electrons and atoms around each iron or sulfur atom is substantially the same in marcasite as in pyrite, the writer has worked out a structure for the former substance which is in complete conformity with the known facts.

The arrangement of iron atoms around each S–S group is shown in Fig. 1 *B*. By comparing corresponding points (denoted by the same letters in the two diagrams) in Figs. 1 *A* and 1 *B*, it may be readily seen that the relative positions of atomic centers are practically the same in the two crystals. In Fig. 2 all the atoms and bonds in the unit parallel-

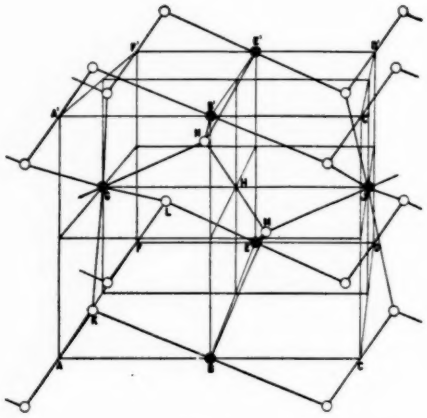

Fig. 2.

Marcasite.

opiped are represented. (The lettering corresponds to that in Figs. 1 *A* and 1 *B*.) The structure may be described as being composed of two interpenetrating lattices, one of which contains an iron atom at the corners and the center of the unit cell, and the other a pair of sulfur atoms at the corners and the center of the unit cell. Each of these

[1] J. Am. Chem. Soc., "Electronic Structures of Crystals. I," soon to be published.

[2] G. N. Lewis, idem, *38*, 762 (1916).

[3] Huggins, idem., "Electronic Structures of Atoms," soon to be published.

lattices is in turn made up of two interpenetrating lattices in which the iron atoms or the pairs of sulfur atoms are at the corners *only* of the unit cell, the difference between the two iron lattices or the two sulfur lattices being in the orientation of the atoms at the points of the lattices. The symmetry of the structure is such as to produce crystals belonging to the bipyramidal class of the orthorhombic system. Each iron atom is bonded to six sulfur atoms and each sulfur to three iron and one other sulfur atom.

The axial ratio of the marcasite crystal [1] has been given as $a : b : c = 0.7646 : 1 : 1.2176$. Preliminary calculations indicate that the distances AB, AF and AA' (Fig. 2) are in this proportion. Since the unit distance in the a direction is AC, rather than AB, the correct axial ratio is $a : b : c = AC : AF : AA' = 1.5292 : 1 : 1.2176$.

Bragg[2] has determined the distance GH (Fig. 1 A) in pyrite as 2.69 Å. (1 Ångstrom = 10^{-8} cm.). If now we assume the corresponding distance ($GH = AB$, Figs. 1 B and 2) in marcasite to be the same, then twice this, or 5.38 Å., is a, and the volume of the unit parallelopiped $ACDFA'C'D'F'$ is

$$5.38 \text{ Å.} \times \frac{5.38 \text{ Å.}}{1.5292} \times \frac{1.2176 \times 5.38 \text{ Å.}}{1.5292} = 81.08 \text{ Å.}^3$$

Since there are four sulfur atoms and two iron atoms in this parallelopiped, half of this, or 40.54 Å., is the volume per molecule. Multiplying by Avogadro's number gives the molal volume, and dividing the molecular weight by the molal volume gives the density, in grams per c.c.,

$$D = \frac{119.96}{0.6062 \times 10^{24} \times 40.54 \times 10^{-24}} = 4.882.$$

This is in good agreement with the observed density, which Groth gives as 4.85–4.88 g./c.c.

Distortions of the Atoms.—The distance BH ($= AG$) may be calculated, from the axial ratio and the value $AB = 2.69$ Å., to be 2.77 Å., which is somewhat greater than the corresponding distance AB. This may be accounted for as follows:

$\angle KGL$ must equal $\angle BME$. Now G is an iron atom bonded to six sulfur atoms, the bonds tending to form central angles of 90° with each other, while M is a sulfur atom bonded to four other atoms, the bonds tending to make a somewhat greater angle with each other (109° 28′ if the bonds were all identical). In pyrite the corresponding angle (*e.g.*, $\angle BME$, Fig. 1 A) between two S–Fe bonds is about 117°. We might

[1] Allen, Crenshaw, Johnston, and Larsen, Zeit. f. anorg. Chem., *76*, 201 (1912).

[2] Loc. cit.

then expect the angles KGL and BME to be between 90° and 117°, and such is the case. We may approximate their value by assuming the distance HM and the angle MHJ to be the same as the corresponding distance and angle in pyrite. $\angle BME$ may then be computed to be 102° 10′. From this, BM is 2.26 Å. and $\angle HMB$ is 108° 05′.

This last angle is several degrees greater than the Fe–S–S angle (Fig. 1, $\angle HMB = 102°$) in pyrite, and it is largely for this reason that HB is greater than AB. Also, because the tetrahedra of electronpairs around the sulfur atoms and the octahedra of pairs around the iron atoms are considerably distorted, the distances between atomic centers are probably slightly greater than if the arrangement were perfectly regular.

Arsenopyrite and Loellingite.—It is interesting to compare the dimensions of arsenopyrite (FeAsS) and loellingite ($FeAs_2$) with those of marcasite. These, as well as a number of other minerals,[1] are in the same crystallographic class as marcasite and in all probability they possess similar structures, arsenic atoms replacing half or all of the sulfur atoms.[2]

Assuming that this is the case, it is possible to compute from the densities and axial ratios of the crystals the dimensions of the unit cells. These are given in Table I. The data are taken from Groth's Chemische

TABLE I.

	FeS_2.	FeAsS.	$FeAs_2$.
Density (g./c.c.).....	(4.88)	6.12–6.18	7.40
Molec. volume.....	40.5 Å.^{3}	43.6 Å.^{3}	45.8 Å.^{3}
$a : b : c$.....	1.5292 : 1 : 1.2176	1.3546 : 1 : 1.1882	1.3378 : 1 : 1.2331
$\frac{a}{2} = AB$.....	2.69 Å.	2.57 Å.	2.55 Å.
$b = AF$.....	3.52 Å.	3.79 Å.	3.82 Å.
$c = AA'$.....	4.28 Å.	4.51 Å.	4.71 Å.
$AG = BH$.....	2.77 Å.	2.945 Å.	3.025 Å.

Krystallographie, Vol. 1. For FeAsS the average value of the density is used. Groth's a is taken as $a/2$ in each case. The distance $AG = BH$ is also given, for comparison with AB.

It will be noted that the unit distance in the a direction actually decreases when arsenic replaces sulfur in the crystal, although without doubt the "radius" of the arsenic atom in crystals is greater than that

[1] Cf. Wherry, J. Wash. Acad. Sci., *10*, 487 (1920).

[2] The Braggs have shown that cobaltite, CoAsS, has the same type of structure as has pyrite. (X-rays and Crystal Structure, p. 154.)

of the sulfur atom.[1] On the other hand the replacement of sulfur by arsenic causes a considerable increase in the dimensions of the structure in the b and c directions. This can be interpreted as meaning that the As–S and As–As axes (NM) are more nearly normal to the basal planes than are the S–S axes. In other words, $\angle MHJ$ is greatest in $FeAs_2$ and least in FeS_2.

It is probable also that the atomic radius of iron—the distance from atomic center to valence pair—is slightly different in these compounds due to the fact that the charge on the atomic kernel is different in the three cases. In FeS_2 each iron atom furnishes two electrons to the valence bonds around it, in FeAsS three, and in $FeAs_2$ four, assuming each sulfur atom to furnish six and each arsenic five; for, as has already been stated, fourteen electrons per "molecule" are needed.

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[1] W. L. Bragg, Phil. Mag. (6), *40*, 169 (1920), gives 1.02 Å. for sulfur and 1.26 Å. for arsenic.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

MINUTES OF THE ANNUAL MEETING, TORONTO, DECEMBER 28–30, 1921.

THE twenty-third annual meeting (the 112th regular meeting) of the American Physical Society was held in Toronto on December 28, 29 and 30, 1921, in affiliation with Section B—Physics—of the American Association for the Advancement of Science. Meetings were held in the lecture room of the Physical Laboratory at the University of Toronto. The attendance was about one hundred and fifty at the ordinary sessions; on Thursday, December 29, there was a joint session with Sections B and C, and the American Mathematical Society, the attendance then being about two hundred. On the evening of Friday, December 30, there was a dinner of the affiliated societies attended by about one hundred members and friends. The arrangements made by the local committee for the entertainment of the members were most excellent and the meeting was generally considered one of the most enjoyable that the Society has ever held.

The president of the Society, Theodore Lyman, presided at all sessions of the Society.

On the afternoon of Wednesday, December 28, 1921, the president of the American Physical Society, Professor Theodore Lyman, gave the official address on "The Spectroscopy of the Extreme Ultraviolet."

On the morning of Thursday, December 29, 1921, there was a joint session with the American Mathematical Society and Sections B and C of the American Association for the Advancement of Science. The presiding officers were G. W. Stewart, chairman of Section B, and W. D. Harkins, chairman of Section C. At this session Professor J. C. McLennan, the retiring vice-president and chairman of Section B, gave an address on "Atomic Nuclei and Extra-Nuclear Electronic Configuration." This address was followed by a Symposium on the Quantum Theory with the following speakers:

For Section C of the A. A. A. S., R. C. Tolman, The Fixed Nitrogen Research Laboratory, Washington.

For the American Mathematical Society, H. B. Phillips, Massachusetts Institute of Technology.

For the American Physical Society, Saul Dushman, General Electric Company.

The regular annual business meeting of the American Physical Society was held on Friday morning, December 30, 1921, at 11 o'clock. A canvass of the

ballots for Officers resulted in the election of the following officers for the year 1922:

For President: Theodore Lyman.

For Vice-President: C. E. Mendenhall.

For Secretary: D. C. Miller.

For Treasurer: G. B. Pegram.

For Members of the Council, four-year Term: H. G. Gale and D. L. Webster.

For Members of the Board of Editors of THE PHYSICAL REVIEW, *three-year term:* A. J. Dempster, E. P. Adams and A. L. Hughes.

At the meeting of the Council held on December 30, 1921, twenty-nine persons were elected to membership, seven were elected to fellowship and four were transferred: *Elected to Fellowship:* Kelvin Burns, Paul T. Epstein, Griffith C. Evans, Kyotoku Fuji, Victor Hess, Joel H. Hildebrand, and F. H. Norton; *Transferred to Fellowship:* Edward Bennett, Arthur J. Dempster, A. H. Patterson, Joseph Valasek; *Elected to Membership:* Hugh M. Ackley, L. M. Alexander, Ernest F. Barker, Perry Byerly, Jr., Herbert Kimball Cummings, John C. Deagan, Joseph W. Ellis, K. C. Fang, Chas. M. Heck, T. R. Hogness, Robert J. Hopkins, Douglas E. Howes, M. L. Huggins, Laurence M. Klauber, Hubert Mann, Charles R. Moore, Wayne B. Nottingham, Marcus D. O'Day, John Patterson, Clarence C. Schmidt, Paul John Searles, Russell E. Seidle, Hugo F. Sloctemyer, Raymond R. Starke, Wilson Taylor, Harold M. Terrill, Andrew Thomson, Yu Tai Yao, and Mr. Zanstra.

The Secretary reported the deaths of nine members and the resignations of seven. The membership at the present time consists of 7 honorary members, 461 fellows and 925 members, making a total of 1393.

By unanimous vote the Society adopted the following resolution which had been favorably reported by the Council:

Resolved: That the American Physical Society believes that it is inimical to the progress of American science and to the development of American industry to curtail the privilege of duty-free importation of books and scientific apparatus which educational institutions have heretofore enjoyed under all administrations.

The regular scientific program consisted of seventy-seven contributed papers, nine of which were read by title. The abstracts of all papers will be found on the succeeding pages. The program was as follows:

The State of Polarization of Light Diffracted at Large Angles from Straight Edges of Different Material. J. M. KUEHNE, University of Texas.

An Experimental Method for Determining Quantitatively Under Given Conditions, the Relative Influence of Radiation and Convection in the Transfer of Heat Through Moving Air. L. H. NICHOLS, McGill University. (Presented by A. N. Shaw.)

Geometrical Proof for the Wadsworth Constant-Deviation System. R. C. GIBBS and J. R. COLLINS, Cornell University.

A Piezo-Electric Method for Generating Electric Oscillations of Constant Frequency. W. G. CADY, Wesleyan University.

The Dissipation of Heat in Air from Plain and Blackened Brass Surfaces for Moderate Temperature Differences. T. S. TAYLOR, Westinghouse Electric & Manufacturing Company.

Radiation Equilibrium in an Opaque Uniformly Heated Solid and Duane's Hypothesis as to its Origin. A. G. WORTHING, Nela Research Laboratories.

An Increase in Density in Thin Films. ELIZABETH R. LAIRD, Mount Holyoke College.

Electrical Resistance of a Rotating Coil. A. P. CARMAN, University of Illinois.

The Departure from Ohm's Law in Gold and Silver at High Current Densities. P. W. BRIDGMAN, Harvard University.

Mutual Impedances of Grounded Circuits. GEORGE A. CAMPBELL, American Telephone and Telegraph Company.

Contact Electromotive Forces Due to Films on Metallic Surfaces. A. E. HENNINGS, The University of British Columbia.

Resistance and Thermo-Electric Power of Metallic Germanium. C. C. BIDWELL, Cornell University.

The Production of an E.M.F. on Closed Circuit, by a Light Effect on Argentite. H. HORTON SHELDON and PAUL H. GEIGER, University of Michigan.

Demonstration of the Wind in the Corona Discharge. JAKOB KUNZ, University of Illinois.

Increased Ionization Over Solar Faculae. CHARLES E. ST. JOHN, Mount Wilson Solar Observatory.

A Note on Missing Spectra. A. S. EVE, McGill University.

The Ultra-Violet Absorption of Anthracene and Benzene. J. M. HYATT, Cornell University.

The Ultra-Violet Transmission of Boiled Absolute Ethyl Alcohol. W. R. ORNDORFF, R. C. GIBBS and M. SCOTT, Cornell University.

The Absorption by Water Vapor of Radiation of Wave Lengths Near 6 μ. W. W. SLEATOR and E. R. PHELPS, University of Michigan.

The Infra Red Absorption Spectra of Diatomic Gases and their Ionization Potentials. EDWIN C. KEMBLE, Harvard University.

The Effect of Certain Dissolved Substances on the Infra Red Absorption of Water. J. R. COLLINS, Cornell University.

The Absorption Spectrum of Hydrogen Chloride at 200° K. B. J. SPENCE and C. HOLLEY, Northwestern University.

Two New Lines in the Aluminum Spectrum and their Possible Series Relations. G. D. SHALLENBERGER, University of Chicago.

The Aspherical Nucleus Theory Applied to the Principal Series of Helium. LUDWIK SILBERSTEIN, Eastman Kodak Company.

A Physical Explanation of the Action of the New Singing Tube. CHAS. T. KNIPP and JAKOB KUNZ, University of Illinois.

Theory of Acoustic Wave Filters: The Limiting Frequencies of Transmission. G. W. STEWART, The State University of Iowa.

Diffraction Effects in Sound Absorption Measurements. PAUL E. SABINE, Wallace Clement Sabine Laboratory.

Analysis of the Energy Distribution in Speech. I. B. CRANDALL and DONALD MACKENZIE, Western Electric Company.

The Separation of the Element Chlorine into Isotopes (Isotopic Atomic Species). WILLIAM D. HARKINS and ANSON HAYES, University of Chicago.

On the Determination of Surface Thermal Conductivities. LETHA A. SMITH, McGill University. (Presented by A. N. Shaw.)

The Causes of Reaction Expansion in Amalgams. ARTHUR W. GRAY, The L. D. Caulk Company.

The Porous Plug Coefficient for Air. J. R. ROEBUCK, University of Wisconsin.

Ether-Drift Experiments at Mount Wilson Observatory. DAYTON C. MILLER, Case School of Applied Science.

Photo-Elasticity or Optical Investigation of Stress Distribution in Solid Bodies. PAUL HEYMANS, University of Ghent, Belgium.

Experiments on the Sign of the Electric Charge Assumed by a Metal Immersed in a Liquid. R. D. KLEEMAN and WILLIAM FREDRICKSON, Union College.

The Analysis of Simple Periodic Curves by a Projection Method with Special References to Estuary Tidal Problems. E. V. HENRY, McGill University. (Presented by A. N. Shaw.)

A Galvanometer Method for Producing at a Distance a Magnified Record of a Mechanical Motion. F. WENNER, Bureau of Standards.

The Influence of Small Variations in the Outlet of a Smooth Brass Tube on the Distribution of Static Pressure When Air is Flowing Through the Tube. T. S. TAYLOR, Westinghouse Electric & Manufacturing Company.

Cohesion and Adhesion. WILSON TAYLOR, University of Toronto.

Progress of Work with the Crystelliptometer on Selenium Crystals. LEROY D. WELD, The State University of Iowa.

The Transmitted Effect in Selenium Crystals. J. C. POMEROY, Bethany College.

Further Experiments on Critical Potentials in Hydrogen. F. L. MOHLER, PAUL D. FOOTE and E. H. KURTH, Bureau of Standards.

Photo-electric Phenomena in Coated-filament Audion Bulbs. R. C. GIBBS and EDNA L. MEACHAM, Cornell University.

The Information Service of the National Research Council. ROBERT M. YERKES, National Research Council.

Power Factors in Radio Circuits. N. H. WILLIAMS, University of Michigan.

"J" Radiation: A Summary. F. K. RICHTMYER, Cornell University.

The Dilemma of the Helium Atom. JOHN H. VAN VLECK, Harvard University.

Moment of Momentum of Magnetic Electrons. E. H. KENNARD, Cornell University.

Theory of Ionization by Cumulative Action. K. T. COMPTON, Princeton University.

A Significant Exception to the Principle of Selection. PAUL D. FOOTE, F. L. MOHLER and W. F. MEGGERS, Bureau of Standards.

The Charge on the Alpha Particle. J. E. SHRADER, Westinghouse Electric & Manufacturing Company.

Radiation from a Group of Electrons. LEIGH PAGE, Yale University.

A Magnetic Fall of Potential Method for Testing Short Bars of Iron. ARTHUR W. SMITH, University of Michigan.

A New Method for the Determination of the Magnetic Susceptibilities of Gases. JAKOB KUNZ and E. C. FRITTS, University of Illinois.

A Sine Galvanometer for Determining in Absolute Measure the Horizontal Intensity of the Earth's Magnetic Field. S. J. BARNETT, Carnegie Institution of Washington.

Results of Comparisons of Instruments for Measuring the Earth's Magnetic Elements. LOUIS A. BAUER and J. A. FLEMING, Carnegie Institution of Washington.

Further Results of Line Integrals of the Earth's Magnetic Force. LOUIS A. BAUER and W. J. PETERS, Carnegie Institution of Washington.

Characteristic X-Rays from Light Elements. A. LL. HUGHES, Queen's University.

Energy Relations Between X- and β-Rays. J. A. GRAY, McGill University.

Positive-Ray Analysis of Zinc and Calcium. A. J. DEMPSTER, University of Chicago.

The Effect of Dissolved Substances on the Deposition of Colloidal Particles from a Solution by Means of an Electric Current. RICHARD D. KLEEMAN, General Electric Company.

The Effective Range of β-Rays. J. A. GRAY and A. V. DOUGLAS, McGill University.

On the Spectrum of the γ-Rays from Radium B and C. ALOIS F. KOVARIK, Yale University.

The Beginning of the K and L Series of X-Rays. F. L. MOHLER and PAUL D. FOOTE, Bureau of Standards.

Secondary X-Rays From Crystals. G. E. M. JAUNCEY, Washington University.

Brightness of Tungsten. W. E. FORSYTHE, Nela Research Laboratories.

The Luminescence of Solidifying Antimony. E. KARRER, Nela Research Laboratories.

The Thermionic Work Function of Tungsten. C. DAVISSON and L. H. GERMER, Western Electric Company.

A Spectroscopic Method for Determining the Effective Temperature of Absorbing and Emitting Molecules. RAYMOND T. BIRGE, University of California.

The Excitation of the Enhanced Spectra of Sodium and Potassium in a

Low Voltage Arc. PAUL D. FOOTE, W. F. MEGGERS and F. L. MOHLER, Bureau of Standards.

The Significance of the $\frac{1}{2}$ Terms in Spectral Series Formulæ. PAUL D. FOOTE and F. L. MOHLER, Bureau of Standards.

A Method for Increasing the Carrying Capacity of a Rheostat. W. E. FORSYTHE, Nela Research Laboratories.

A Transition or Absoıption Layer Theory of the E.M.F. of the Voltaic Cell. RICHARD D. KLEEMAN, Union College.

Quantum Theory of Photographic Exposure. LUDWIK SILBERSTEIN, Eastman Kodak Company.

The Physical Constituents of the Atmosphere of Venus. CHARLES E. ST. JOHN and SETH B. NICHOLSON.

The Separation of Mercury into Isotopes. WILLIAM D. HARKINS and R. S. MULLIKEN.

The Crystal Structure of Mercury. L. W. McKEEHAN and P. P. CIOFFI.

The abstracts of the papers on the above program are given in the following pages.

DAYTON C. MILLER,
Secretary.

THE STATE OF POLARIZATION OF LIGHT DIFFRACTED AT LARGE ANGLES FROM STRAIGHT EDGES OF DIFFERENT MATERIAL.

BY J. M. KUEHNE.

THE light diffracted at considerable angles (5° to 25° and more inside the geometrical shadow) is of different states and degrees of polarization according to (*a*) the angle of diffraction, (*b*) the "sharpness" of the edge, and (*c*) the material of the edge. To avoid the influence of "sharpness" (which affects principally the amount of diffracted light under otherwise identical conditions) thin plates of uniform thickness (.15 mm.) and carefully rounded edges were used.

Part of the spectrum from a carbon arc was polarized at an azimuth of 45° and focused on the diffracting edge, which was mounted coincident with the axis of a spectroscope. The diffracted light was examined by means of a long focus microscope which was mounted in place of the telescope, and focused on the diffracting edge. The microscope was equipped with an analyzing nicol and a quarter wave plate.

Dielectric diffracting edges produce a rotation of the plane of polarization of from 0° to 8° or 10° for diffracting angles varying from 0° to 20° or 25° inside the geometrical shadow; the electric vector perpendicular to the edge being the stronger.

Metallic diffracting edges produce very marked elliptical polarization, being distinguished in this respect from dielectric edges. This shows that the vector parallel to the edge, in addition to being more absorbed, is retarded in phase, relative to the vector perpendicular to the edge. This phase retardation varies with different metals and increases with the diffraction angle.

Of the metals so far investigated nickel, aluminum and iron have shown this effect most strongly. In the case of nickel at a diffraction angle of 25° the phase retardation is as much as 90°.

More complete data covering a wider range of materials will be published shortly.

UNIVERSITY OF TEXAS,
AUSTIN, TEXAS,
December 9, 1921.

AN EXPERIMENTAL METHOD FOR DETERMINING QUANTITATIVELY UNDER GIVEN CONDITIONS, THE RELATIVE INFLUENCE OF RADIATION AND CONVECTION IN THE TRANSFER OF HEAT THROUGH MOVING AIR.

BY L. H. NICHOLS.

BY using a pair of slightly modified kata-thermometers,[1] it has been found that the influences of incident heat radiation and of turbulent atmospheric conditions on the transfer of heat to a given place of observation, can be estimated separately and quantitatively over a considerable range of conditions. The experimental procedure consists fundamentally in sorting out these factors by means of their influence on the rate of cooling of previously calibrated models for which the kata-thermometers will serve very conveniently.

Four main operations are necessary; the first of which will suffice indefinitely for the particular instrument calibrated.

1. The preliminary calibration consists primarily of the determination in vacuo, and again in stagnant air of the rates of cooling of the katas (or particular instruments used) when surrounded by large dark enclosures and over the range of temperatures subsequently to be investigated.

2. At the place of testing, the rate of cooling of an ordinary dry kata is obtained in the usual manner.

3. Simultaneously or under similar conditions, the rate of cooling of a dry kata which has been silvered and polished is observed.

4. The apparent temperature of the air is taken by means of a screened thermometer at the place of observation.

By applying the results of previous calibration it is possible to express the quantities measured in terms of units of heat flowing per unit of time. Also by the process of subtraction it is possible to obtain from the results of these operations (1) the influence of incident radiation which arises from sources at higher temperature than that of the surrounding air; (2) the influence of any existing wind, ordinary ventilation, or turbulence as distinct from that of convection in still air.

The validity and practical applicability was tested satisfactorily in the

[1] Hill, Griffith and Flack, "The Measurement of the Rate of Heat-loss at Body Temperature by Convection, Radiation and Evaporation." *Phil. Trans. Roy. Soc.*, B, Vol. 207, p. 201 (1915).

following manner. Readings as outlined above in 2, 3, and 4 were taken in a dark room in the direct paths of radiation from an electric heater, and of wind from a fan, and it was possible by means of these observations and previous calibrations, to predict successfully the readings corresponding to the cases when either the heater or the fan or both of them were removed.

The applications of this method are numerous. In particular it should be possible to allow completely for the influence of solar radiation and atmospheric turbulence upon the readings of various instruments which are at present considered unreliable under open air conditions. The comparative analysis of heating by radiation and heating by convection has important physical bearings and may be facilitated by measurements of this kind.

McGill University.

Geometrical Proof for the Wadsworth Constant Deviation System.

By R. C. Gibbs and J. R. Collins.

By an analytical method Wadsworth,[1] determined the location of the axis of rotation of a constant-deviation prism-mirror system such that the emergent ray remains fixed in position as the system is rotated. This proof involves a series of long though simple transformations.

The location of this axis can be determined by a short geometrical proof similar to that used by E. Bloch,[2] in finding the corresponding axis of rotation for a constant deviation prism of the Pellin-Broca type.

Cornell University,
December, 1921.

A Piezo-Electric Method for Generating Electric Oscillations of Constant Frequency.

By W. G. Cady.

In a former communication[3] several methods were described whereby the frequency of a vacuum-tube oscillating circuit could be rendered very stable by the use of a piezo-electric resonator of proper dimensions. Further investigation has shown that it is possible, with the aid of amplifiers, to make the piezo-electric resonator serve as a *mechanically tuned feedback*, so that a high-frequency alternating current is generated, whose frequency is determined solely by the mechanical vibrations of the quartz plate. The plate is so mounted as to vibrate freely longitudinally between two pairs of close-fitting metallic "coatings." The first pair of coatings is connected between the output anode of a three-stage resistance amplifier and ground, while the second pair is connected between the input grid and ground.

[1] Astronomy and Astro Physics, Vol. 13, p. 835, 1894.

[2] Journal de Physique, Vol. 7, p. 145, 1917.

[3] Physical Review, 18, p. 142, 1921. A more complete account of these experiments, together with the theory of the piezo-electric resonator, will appear in the Proceedings of the Institute of Radio Engineers.

Any slight increase in potential of the output anode alters the electric field between the first pair of coatings, and sets the resonator into vibration. The charges thereby excited in the second pair vary the potential of the input grid. This varying potential, by virtue of the amplification taking place in the system, will, if the proper coating is connected to the grid, still further increase the potential variations of the output anode and thus maintain the vibrations of the resonator. The power output is of course very small—of the order of 1/20 watt—but this small power may of course be further amplified. Maximum power is obtained by tuning the output circuit by means of a variable condenser and inductance in parallel. If the resonator functions properly, however, the frequency is found to be practically independent of the electrical constants, the current merely passing through a maximum when in electrical resonance. The forced vibrations which the resonator executes have a frequency which is not entirely without influence from external circumstances; yet it hardly ever differs from the natural frequency of the resonator by more than one part in 10,000, and for wide ranges of the various parameters of the circuit the variation is very much less than this.

By the use of quartz plates 3 cm. long, frequencies of (roughly) either 100,000 or 200,000 may be obtained. I have not yet succeeded in obtaining regeneration with frequencies much higher than these. For frequencies so low that it is impracticable to use quartz plates of sufficient length, flat steel rods have been successfully employed. Such a rod has a small quartz plate cemented to each side at its center, and each of the quartz plates is provided with two separate tinfoil coatings. In this case a five-stage amplifier has been found necessary for regeneration. The frequency is essentially that of the steel rod, the quartz plates serving merely to excite longitudinal vibrations in the steel.

WESLEYAN UNIVERSITY,
MIDDLETOWN, CONN.

THE DISSIPATION OF HEAT IN AIR FROM PLAIN AND BLACKENED BRASS SURFACES FOR MODERATE TEMPERATURE DIFFERENCES.

BY T. S. TAYLOR.

OBSERVATIONS have been made in air, free from convection currents other than those set up by the apparatus itself, of the loss of heat from a flat heater when its surfaces were plain brass and when blackened, for various temperature differences and angular positions relative to the vertical. The energy put into the heater was varied till temperature excesses of the heater's surface were obtained up to 130° C. The surface temperatures were obtained by small copper-constantan thermocouples peened into the metal surface. By temperature excess is meant the difference between the temperature of the heater and that of the surroundings and in particular that of the air before it came into the field of influence of the heater.

Assuming black body radiation for the blackened surface, the heat losses

for various temperature differences were calculated for both radiation and convection. For a temperature difference of 100° C., the following relative values were obtained for the different losses per unit area.

1. Total loss from blackened surface	100
2. Total loss from plain brass surface	55.5
3. Loss due to radiation alone from blackened surface (assuming black body radiation)	62.7
4. Convection loss alone. (This is assumed the same for both surfaces for the same temperature difference)	35.8
5. Difference between blackened and plain	44.5
6. Radiation alone from brass surface	17.1

The differences obtained between the losses from the heater used $8\frac{3}{4}'' \times 8\frac{3}{4}'' \times \frac{3}{4}''$ when placed at various angles were practically no greater than those due to experimental variations. This is true also concerning the differences between the temperatures of the heater surfaces.

WESTINGHOUSE RESEARCH LABORATORIES.

RADIATION EQUILIBRIUM IN AN OPAQUE UNIFORMLY HEATED SOLID AND DUANE'S HYPOTHESIS AS TO ITS ORIGIN.

BY A. G. WORTHING.

WHETHER or not the *natural radiation* from the ultimate sources of radiation in an opaque uniformly heated solid agrees in spectral distribution with the *equilibrium radiation* in their immediate neighborhood depends on the optical constants of the solid. The condition for agreement is constancy in κ/λ, where κ (often written nk) is the extinction coefficient and λ the wave-length in vacuo. A considerable tendency toward constancy exists in the measured values of this ratio. Possibly the variations found are real but analogous to those experienced in atomic heats in their relation to Dulong and Petit's law. Whatever the explanation, known difficulties due to surface transition layers seem to justify a tentative assumption of constancy for the purpose of testing theories of the origin of radiation.

Duane's hypothesis, a generalization from X-ray observations, ascribes all radiation to the bombardment of atoms by moving electrons—in the ordinary temperature radiations of incandescent solids, the free electrons connected with electric conduction. Starting with three fundamental assumptions, Duane concluded that Planck's distribution law results. Apparently, however, he overlooked the fact that the coefficient A in his statement of Maxwell's law is in general a function of temperature. Fortunately, however, thermionic emission experiments seem to indicate that the concentration of the free electrons in a solid varies in such a fashion, at least for low concentrations and high temperatures if not in general, as to render the coefficient A constant for this special case.

It is to be inferred from Duane's derivation that the natural radiation from the ultimate sources has the characteristics of black body radiation for free

space. This is almost certainly not the case. Black radiation in free space differs from the equilibrium radiation in an opaque solid, and only in case κ/λ is constant as stated above, has this equilibrium radiation the same spectral distribution as the natural radiation from the ultimate sources. Assuming the constancy of κ/λ and thus for the natural radiation the same spectral distribution as for equilibrium radiation, it seems necessary to modify Duane's assumption (3) so as to read "*the energy radiated per hit is on the average proportional to the fourth power of the speed of the free electron and to the square of the index of refraction for the radiation emitted.* In other words,[1] *the ratio of the energy radiated per impact to the kinetic energy of the impacting electron is proportional on the average to the square of the ratio of the velocity of propagation of the radiation in the solid to that in vacuo.* On the new basis Planck's equation follows without question as to applicability.

In addition to giving certain indications regarding the application of Maxwell's law to free electrons, and pointing out the possibility of a constancy in κ/λ, the discussion shows how Duane's hypothesis, when combined with an assumption of such constancy and with conclusions arrived at independently in other lines of research, gives a satisfying physical concept of processes which may underlie the emission of radiation by its ultimate sources.

NELA RESEARCH LABORATORIES,
NELA PARK, CLEVELAND, OHIO.

AN INCREASE IN DENSITY IN THIN FILMS.

BY ELIZABETH R. LAIRD.

SOME phenomena noted while working with thin celluloid films seemed to indicate that the weight was not proportional to the thickness as determined by an interferometer. Since a number of observers give the thickness of similar films without details as to method of determination, it was decided to investigate the point. For this purpose it was necessary to measure the index of refraction of films of various thickness, the displacement of fringes in an interferometer, the area of the films, and their weight.

It was attempted to measure the index of refraction by a critical angle method by depositing a thin film directly on one side of a glass prism, or by using it as one side of a thin cell with carbon bisulphide as the liquid in between. As far as it went this method indicated no change in the index of refraction with increasing thinness, but in the first case the films made perfect contact with the glass only in little spots, and in the second such a small amount of light was refracted into the prism that an accurate setting with a spectrometer was impossible. The method of using the polarizing angle for this determination proved very convenient, as the same film could be used in this as in the other measurements. The index of refraction found thus showed very little change if any from thick films down to the thinnest used. The index found was between 1.50 and 1.51.

[1] As reworded by the writer's colleague, Dr. E. Q. Adams.

The optical thickness was measured by the fringe displacement in a small Michelson interferometer by noting first the displacement of the central black fringe in white light, then changing to sodium light and noting the displacement of a number of fringes for different positions of the film in order to get an average thickness. The area of the films was found by measuring with a planimeter the hole from which they were cut. The early weighings were made on an ordinary balance sensitive to 0.05 mg., the later by observing in a tele-microscope the displacements of a glass thread clamped at one end and suitably protected from draughts, when the films were placed in a stirrup forming part of the thread. With this weighings could easily be made to 0.005 mg.

The later results were in general agreement with the earlier, and assuming the optical thickness as the true thickness, show that while the density down to a thickness of 400 $\mu\mu$ remains approximately 1.41 grams per cm.^{3}, somewhere below this it begins to increase so that in the neighborhood of 60 $\mu\mu$ it is about 2 and at 30 $\mu\mu$ about 2.5 and that it is higher still at smaller thicknesses. It is expected to continue the experiments.

MOUNT HOLYOKE COLLEGE.

ELECTRICAL RESISTANCE OF A ROTATING COIL.

BY A. P. CARMAN.

THE coil is wound on a circular disk and the disk is rotated at a high speed about its axis. The centrifugal force is thus at right angles to the wire, and if "the electric current has a true momentum" (using Maxwell's words), it might be forced to the outer part of the cross-section of the wire. The experiment is made to determine if this cross-centrifugal force produces any change in the electrical resistance of the coil. The experiment was made in 1913–1914,[1] but gave no results because of a lack of a satisfactory means of making electrical connection with the rotating coil. A year ago a successful method of connecting with such a moving coil was devised;[2] this was described in a paper before this Society at the preceding, Chicago, meeting. From the center of each end of the shaft a fine wire is stretched in the line of the axis of the shaft extended. The wire is about 25 centimeters long and ends in a small swivel and a spring to keep the wire straight. The wire can thus rotate with the shaft, and even when the shaft is totating at 7,000 r.p.m. for considerable time, there is little twist in this axial connecting wire. The wire runs through a mercury trough, passing loosely through end corks, and connection to the outside circuit is made by means of the mercury. To avoid thermo-electromotive forces, connection to the coil was not made through the shaft, but through an insulated tapered plug, and then by an insulated wire which was carried through a hole along the axis of the shaft. Potentiometer tests

[1] Thesis of P. L. Bayley, June, 1914, MS. in University of Illinois Library.

[2] Thesis of C. C. Schmidt, 1921.

showed that the thermal e.m.f.'s in the circuit were less than two millionths of a volt, that is, were negligible. The coil on the disk can be quickly cut out by a short-circuit, and thus the resistance changes in this connection can be measured and allowance made for it. These resistance changes between conditions of rest and of rotation were, under normal conditions, thousandths of an ohm or less, and the changes were not greater for high speeds. The following are random examples of these resistance changes.

	Ohms.				
R. at rest	.1248	.1244	.0733	.0724	.0729
R. rotating	.1323	.1312	.0724	.0729	.0731
Difference	.0075	.0068	.0009	.0005	.0002

A disk wound with copper wire was the first one prepared, but it was found to be so sensitive to temperature effects that all other resistance changes were masked. The next disk was wound with "advance" wire, this wire having a negligible temperature coefficient for resistance. The disk was turned from vulcanized fiber one inch thick, and twenty-eight layers of No. 25 wire were wound in a groove on the circumference and covered with a layer of sealing wax. The average diameter of the coil was 28 cm. Around the edge of the disk, and over the coil was clamped by brass straps a stout hickory band which had been steamed and formed into a circle. For the final experiments, a steel hoop was fitted over the hickory band. The shaft was mounted on "S.K.F." ball bearings and was driven by a long belt from a two-phase induction motor with step-up pulleys. The resistance of the coil at rest was 235.838 ohms, and at 6,837 r.p.m. the resistance was 236.128 ohms, showing an increase of 0.29 ohm or over one tenth of one per cent. increase after allowing for connection changes. This increase and the increases of resistances at speeds of 1,450, 1,960, 2,450 and 4,960 r.p.m. were exactly proportional to the squares of the speeds, and were evidently due to centrifugal forces. Calculations using the ordinary elastic constants of steel were made for the stretch of the steel binding hoop at the highest speed, this being the limiting stretch of the coil. Assuming that the increase of resistance is proportional to the stretch for these small stretches, it was found that the observed increase of resistance was due in considerable part, if not wholly to stretch. But there were some differences and more decisive results were sought. Hence a coil was prepared with loose zigzag windings. With this arrangement, the wire can straighten itself without change of length and hence without strain, when the binding hoop stretches under centrifugal force. With this new coil the change of resistance from rest to a speed of 7,000 r.p.m. was less than one hundredth of one per cent., and probably not over one thousandth of one per cent. The actual resistance measurements were: at rest, 270.4148 ohms; at 6,934 r.p.m., 270.4176 ohms; at 5,199 r.p.m., 270.4231; or the differences were in the

thousandths of an ohm, probably due to the connections. The diameter of the coil was 28.8 cm., so that tangential speed was about 10 kilometers per second, and v^2/r, the acceleration, was about 4×10^7 cm. per sec. per sec. We conclude that if there is any change of the electrical resistance of this wire due to centrifugal force, the change is exceedingly small.

UNIVERSITY OF ILLINOIS,
December, 1921.

THE DEPARTURE FROM OHM'S LAW IN GOLD AND SILVER AT HIGH CURRENT DENSITIES.

BY P. W. BRIDGMAN.

PREVIOUS attempts to detect a deviation from Ohm's law in metals at high current densities, which is to be expected from electron theory, have failed. The chief source of error in previous measurements has been the uncertain correction for the change of resistance under the heating due to the heavy current. A new method has been developed in which this source of error is absent. The method consists of measuring the resistance simultaneously under a heavy direct current and a small superposed alternating current of acoustical frequency. If Ohm's law fails the resistance to the direct current will be different from that to the alternating current. It is obvious that the large temperature error of previous methods is absent because the temperature is the same to direct and alternating current. There is another source of error, however, due to the small alternations of temperature under the joint action of direct and alternating current. This error becomes vanishingly small at high frequencies, and may be eliminated by making measurements at a number of frequencies and extrapolating to infinite frequency. The extrapolation is secured by a knowledge of the theoretical form of the curve.

The method has been applied to gold and silver leaf; the thickness of the gold varied from 8×10^{-6} to 2×10^{-5} cm., and the thickness of the silver was 2×10^{-5} cm. Current densities of 5×10^6 amp./cm.^{2} were attained. Under these current densities there is an increase of resistance of the order of one per cent. The increase is greater for the thick than the thin gold, as would be expected, and is greater for gold of the same thickness than for silver.

These experiments mean, if metallic conduction takes place by a mechanism like a free-path mechanism, that the free path is much longer than the distance between atomic centers. This is in accord with the theory of metallic conduction which I have previously advanced.

THE JEFFERSON PHYSICAL LABORATORY,
HARVARD UNIVERSITY, CAMBRIDGE, MASS.

MUTUAL IMPEDANCES OF GROUNDED CIRCUITS.

BY GEORGE A. CAMPBELL.

An investigation is being made of the mutual impedances between grounded circuits. In case the frequency and separation do not exceed specified limits,

it has been shown that a good first approximation is obtained by using formulas for the direct current mutual resistance and mutual inductance. Any network of conductors located on the surface of the earth with which it is conductively connected at any number of points will, for direct currents, have self and mutual inductances which are equal to the Neumann integral, extended over the network alone. In other words, that portion of the complete Neumann integral for closed circuits which involves the return currents through the earth, vanishes. The earth is assumed to be flat, of infinite extent, of unit permeability and of uniform conductivity.

AMERICAN TELEPHONE AND TELEGRAPH COMPANY.

CONTACT ELECTROMOTIVE FORCES DUE TO FILMS ON METALLIC SURFACES.

BY A. E. HENNINGS.

IN preliminary experiments preparatory to an investigation of the temperature coefficient of contact electromotive forces between metallic surfaces certain new phenomena have been observed which indicate that the true effect may be completely masked by the formation of films.

The experimental arrangement was such that one of the surfaces could be changed through a wide temperature range, while the other was not changed in temperature, except in so far as this was brought about by radiation from the first surface. The bottom of a brass cylinder projecting into the vacuum chamber served as the first of these surfaces and the second was that of an insulated brass plate in communication with a quadrant electrometer. By means of an electro-magnetic device this latter plate was brought near or away from the bottom of the cylinder. Thus the Thomson method of measuring the contact electromotive force could be applied.

When liquid air was poured into the cylinder and when the vacuum was such as could be obtained with a Gaede mercury pump, but without charcoal absorption, the contact electromotive force between the brass surfaces changed rapidly from + .02 volt at 20° C., to a higher positive value, which changed quickly to a negative value reaching a maximum of − .78 volt. After the liquid air had evaporated and the bottom of the cylinder began to rise in temperature, the contact electromotive force changed, comparatively slowly at first, to a less negative value, but then very abruptly from − .47 volt to + .32 volt between the times of two observations made as quickly as possible. A maximum of + .43 volt was reached in a short time, which, however, gradually fell, approximating the initial value when the whole apparatus approached the temperature of the room. Other series of observations yielded still greater differences between extremes, the total change in one case being between + .28 and − 1.13 volts.

With an improved vacuum the fluctuations were less pronounced, but nevertheless such that no data, purporting to represent the true temperature coefficient of contact electromotive forces, were obtained.

UNIVERSITY OF BRITISH COLUMBIA.

Resistance and Thermoelectric Power of Germanium.

By C. C. Bidwell.

The electrical resistance and the thermoelectric power of a sample of very pure metallic germanium have been determined, simultaneous data on the two properties having been taken from −192° C. to +675° C. A reversible transformation of some sort is indicated by the data. The change begins at about +125° C. and is apparently not completed until at least 550° C. is reached. The thermoelectric power is positive with a positive temperature coefficient from −192° C. to +125° C., the value being approximately +160 microvolts at −192° C. and +425 microvolts at +125° C. With further temperature rise the thermoelectric power diminishes rapidly, changing sign at 300° C. It becomes again a linear function of the temperature from 550° to 675° with a positive coefficient, the value at 550° being about −175 m. v. and at 675°, −125 m. v.

The resistance shows a minumum at —116° C. with a positive temperature coefficient from that temperature to +125°. It goes through a maximum at about +175° C., thereafter dropping with rising temperature to a minimum at +645°. The resistance-temperature law between − 193° and +125° and from 550° to 675°, *i.e.*, where not obscured by the transformation, is of the form $\log R = \alpha/T + \beta T + \gamma$. This is the law which has been shown to hold for many of the oxides and non-metals.

In the transition region there seems to be a solid solution of one form in the other, the relative proportions depending upon the temperature.

The Production of an E.M.F. on Closed Circuit, by a Light Effect on Argentite.

By H. Horton Sheldon and Paul H. Geiger.

While obtaining data on the change of resistance of argentite (Ag_2S) with change of illumination, it was observed that under certain conditions a deflection of the galvanometer was secured on illumination when no external e.m.f. was applied to the circuit. This effect was further studied when the crystal was connected directly to the galvanometer and the direction of the e.m.f. found to depend upon the contact illuminated.

When the lamp was replaced by a heating coil, which radiated a much greater amount of heat than the lamp by a thermopile test, certainly less than one per cent. of the deflection was secured, thereby showing that a true light effect was being obtained. Other experiments resulted in the same conclusion.

The effect of intensity was studied by varying the distance between lamp and crystal and it was found that the e.m.f. produced decreased with distance. With one crystal an e.m.f. of .0125 volt was obtained with a 20-candle power lamp at 12 cm. from the contact. The procedure was complicated by a changing resistance in the crystal.

This light effect was found in over a dozen specimens secured from different regions, as well as in a number of other minerals. However, the effect was more marked in argentite than in any of the other crystals examined.

It was found that the resistance of a crystal of argentite varied from several megohms with a potential difference across the crystal of one volt to less than a hundred thousand ohms with a potential difference of twenty volts. In obtaining the curve showing this relation, it was found necessary to apply the voltage only for a very small fraction of a second for the resistance very rapidly increased with the time that the voltage was applied.

The ratio $\Delta R/R$ (ΔR being the change of resistance on illumination) was found to be a constant for different applied voltages.

UNIVERSITY OF MICHIGAN.

DEMONSTRATION OF THE WIND IN THE CORONA DISCHARGE.

BY JAKOB KUNZ.

THE wind has been demonstrated by means of vapors of ammonium chloride and ether. The deflections of these vapor jets can easily be projected on a screen by means of an arc lamp without lenses. A corona discharge of alternating currents between 2 parallel wires of different diameters has been used. The phenomena presented by 2 different and 2 equal wires are very different.

UNIVERSITY OF ILLINOIS.

INCREASED IONIZATION OVER SOLAR FACULÆ.

BY CHARLES E. ST. JOHN.

ON the Bohr theory, radiation of the normal or arc-type occurs when the nuclear charge is unity and an electron falls from an orbit to one of lower potential energy. The enhanced or spark lines are produced when the nucleus is doubly charged and the atom is first-step ionized. Saha has adapted the Nernst equation for the equilibrium of gaseous reactions to the determination of the percentage of ionized to un-ionized atoms as a function of temperatures and pressure. The Saha equation suggests, as he points out, that in the spectra of faculæ, owing to higher temperature, the percentage of ionization should be increased and hence the enhanced lines strengthened. Preliminary spectrograms of faculæ show changes in the intensity of the enhanced lines in agreement with this deduction, the spectrum changing from Go to F-type, that is in the direction of higher temperature. The preliminary results for titanium are as follows:

Wave-length.	Class of Line.	Effect over Faculæ.
4306.078	Arc	No change
4443.976	Spark	Strengthened
4468.663	Spark	Strengthened
4501.445	Spark	Strengthened
4548.198	Arc	No change
4527.490	Arc	No change
4572.156	Spark	Strengthened

MOUNT WILSON SOLAR OBSERVATORY.

A NOTE ON MISSING SPECTRA.

BY A. S. EVE.

MINING engineers use well-constructed sieves made of phosphor bronze wire with various sizes of mesh, ranging up to three hundred wires to the inch.

When a narrow beam of parallel light falls on the sieve diffraction bands and patterns are produced which may be observed directly, or after projection.

By a calculation involving simple proportion only, the wave-length of any light can be determined.

A sieve with 300 wires to the inch was found to have the intervals between the wires precisely equal to their diameters. It necessarily follows that the even order spectra are entirely absent, while the odd order spectra are enhanced in brilliancy. On inclining the sieve to the ray the gaps are effectively narrower while the circular wires are not, hence at about 30° the missing spectra suddenly appear.

A photograph of the sieve was taken with a white screen behind it. This photograph was used as a grating and all the spectra were found present. Possibly the light flooded the plate when the photograph was taken, so that the gaps were enlarged relatively to the image of the wires. There is no new principle involved in the above, but the method is a valuable and effective method of demonstrating missing spectra. Such sieves might have advantages over coarse gratings in astronomical work.

MCGILL UNIVERSITY.

THE ULTRAVIOLET ABSORPTION OF ANTHRACENE AND BENZENE.

BY J. M. HYATT.

THE purpose of this investigation was to check the results previously obtained, by using the Hilger sector photometer according to the method described by Howe.[1]

Anthracene.

The anthracene absorption was determined by using a number of different concentrations of the anthracene in ethyl alcohol, the thickness of the absorbing

[1] H. E. Howe, PHYS. REV., Vol. VIII., 1916.

layer being 1 centimeter in each case. Ten absorption bands were observed, four of them however were too faint to admit of quantitative measurements of the absorption coefficient. The four intense bands were double, the secondary bands being distinctly visible on the photographic plate.

The figures in the table give the frequency numbers of the absorption bands together with those obtained by Hartley[1] and by Glatzel.[2]

It may be seen from Table I. that there is an approximately constant interval of 150 in the frequencies between the first, third, fifth, etc., bands and an interval of approximately 140 between the second, fourth, etc., bands. The fourteen bands may be represented by two series, series A with a mean frequency interval of 147; and a series B with a mean frequency interval of 142. The third and fourth bands in the table were taken as references and two series were computed with an interval of 147 and 142.

TABLE I.

Hartley	Glatzel.	Observed.	Computed.
2,635	2,620	2,650	2,653
	2,680	2,700	2,698
2,780	2,780	2,800	2,800
	2,840	2,840	2,840
2,915	2,965	2,945	2,947
	3,025	2,990	2,982
3,050	3,100	3,095	3,094
		3,130	3,124
		3,240	3,241
			3,266
			3,388
		3,410	3,408
		3,540	3,535
			3,550
			3,682
		3,688	3,692
			3,829
			3,834
		3,975	3,976
			3,976
			4,123
		4,115	4,118

Benzene.

The absorption of the benzene was determined, using very thin layers of the solutions of benzene in ethyl alcohol. Ten absorption bands were observed, three of them being however very faint.

The position of the ten bands that were found are compared in the Table II. with the position of those that were found by previous observers.

[1] Hartley, Journal Chem. Soc., Vol. 39, 1881.

[2] Glatzel, Physikalische Zeitschrift, Vol. 2, 1900.

TABLE II.

Hartley and Dobbie.[1]	Glatzel.[2]	Baly and Collie.[3]	Observed.
3,710		3,725	3,720
		3,765	3,780
3,833	3,820	3,830	3,830
3,925	3,920	3,915	3,920
4,014	4,010	4,025	4,015
4,109	4,110	4,110	4,120
4,205	4,200	4,200	4,210
			4,295
			4,365
			4,465

CORNELL UNIVERSITY,
December, 1921.

THE ULTRAVIOLET TRANSMISSION OF BOILED ABSOLUTE ETHYL ALCOHOL.

BY W. R. ORNDORFF, R. C. GIBBS AND M. SCOTT.

IN measuring the ultraviolet absorption spectra of two isomers of a certain organic salt when dissolved in absolute ethyl alcohol, it was found that the absorption of a solution of either isomer changed gradually on standing in such a way as to indicate a slow transformation to the other isomer. Although the absorption spectra of the two solutions differed widely when first made up, at the end of six months the absorption of the two had become almost identical.

In attempting to modify the equilibrium thus established between the two isomers in solution, one of the solutions was heated to the boiling point. The absorption of the solution after heating showed that instead of simply changing the ratio of the two isomers the heating had modified the solution in other ways. One possible explanation of the change was that the *solvent* had been modified in some way. The transmission of boiled absolute alcohol was therefore measured and compared with that of freshly distilled absolute alcohol. It was found that for a layer 1 cm. thick the transmission of the boiled alcohol was decidedly less than that of alcohol which had not been heated after distillation from about 0.37 μ to about 0.24 μ (the shortest wave-length studied). The maximum decrease in ratio of transmission for 1 cm. layer was about 90 per cent.

The decrease in transmission increases with the time of boiling up to a certain point. Within small limits the change in transmission is the same for alcohol boiled in flasks made of ordinary glass, pyrex glass, or Jena glass, or in a nickel-plated copper flask. In all these cases the vapor produced by

[1] Hartley and Dobbie, Journal Chemical Soc., 1898.

[2] Glatzel, Physikalische Zeitschrift, Vol. 2, 1900–01.

[3] Baly and Collie, Journal Chemical Society, 1905.

boiling was condensed and returned to the flask. The transmission increases slightly for a few days after the alcohol is boiled. The alcohol condensed from the vapor produced by boiling gave the same transmission as the unboiled alcohol.

It is quite possible that the change in transmission here described is not due to any real change in absorption but to a scattering produced by colloidal particles of the material of the flask or to oxidation of the alcohol.

It is hoped that in the near future experiments can be performed to determine whether scattering or oxidation is the cause of the change in transmission. Similar changes, although somewhat less marked, were found for boiled water and boiled glacial acetic acid.

CORNELL UNIVERSITY,
December, 1921.

THE ABSORPTION BY WATER VAPOR OF RADIATION OF WAVE-LENGTHS NEAR 6 μ.

BY W. W. SLEATOR AND E. R. PHELPS.

THE study of the absorption spectrum of water vapor undertaken a few years ago has been continued, and the analysis of the region of 6 μ has been completed. The new map shows a more complicated structure than was presented before, and proves the existence of many individual lines hitherto only suspected or quite unknown. It is plain however that the number of known lines would be still further increased by higher dispersion. The interest of the work lies in its bearing on the theory of band spectra, the information it supplies about possible series in the water vapor spectrum and the help it may give in problems of molecular structure.

UNIVERSITY OF MICHIGAN.

THE INFRA-RED ABSORPTION SPECTRA OF DIATOMIC GASES AND THEIR IONIZATION POTENTIALS.

BY EDWIN C. KEMBLE.

THE Lenz[1] theory of the infra-red band spectra of gases is simply the straightforward application to molecular rotational and vibrational motion of the Wilson-Sommerfeld quantum conditions, the Bohr frequency principle, and the Bohr principle of selection. Kratzer[2] has recently derived a formula for the frequencies of the lines in the infra-red absorption spectra of diatomic gases in conformity with the Lenz theory, but his method of evaluating the quantum integral for the vibrational motion is open to objection.[3]

Using a method of integration in series described in a previous paper[3] the writer obtains the following new formula for the frequencies in the infra-red

[1] W. Lenz, Verh. d. D. Phys. Ges., 31, p. 632, 1919.

[2] A. Kratzer, Zeit. f. Phys., III., 5, p. 289, 1921.

[3] E. C. Kemble, Proc. Nat. Acad. Sci., 7, p. 283, Oct., 1921.

absorption spectrum of a diatomic gas:

$$\nu_s^n = k_0^{(n)} + k_1 s + k_2^{(n)} s^2 + k_3 s^3 + k_4^{(n)} s^4 + \cdots.$$

Here n, $|s|$ are the vibrational and rotational quantum numbers for the final stationary state, respectively, and 0, $|s \pm 1|$ are the corresponding initial quantum numbers. n is unity for the "fundamental" band, two for the first "harmonic," etc. s is the term number of the line in question reckoned from the component next the center on the red side as zero. The coefficients k_1 and k_3 are independent of n. All the constants are determined in terms of the coefficients in a power series expansion for the potential energy.

The new formula agrees with that of Kratzer for small values of s and n. It may be checked in three ways. There is, in the first place, a definite relation between k_3, k_1, and k_0 which may be verified by an experimental study of these constants. The recent observations of Colby and Meyer[1] on the HCl band at 3.5 μ form a rough, but as yet insensitive check on this requirement of the theory. In the second place, the coefficients k_1 and k_3 should be the same for the harmonic band as for the fundamental. In testing this point the data obtained by Imes[2] for the HCl band at 1.7 μ were used. The agreement is not perfect, but seems to be within the limits of experimental error.

From a sufficiently complete experimental knowledge of the infra-red absorption spectrum of a diatomic gas it is possible by means of this theory to calculate its ionization potential and thus to obtain a third check. The ionization potential of HCl calculated from the available spectroscopic data is 14 volts in close agreement with the experimental vaule obtained by Foote and Mohler[3] and the theoretical value calculated by Born[4]. The spectroscopic data for HBr are neither so complete nor so accurate as for HCl, but a rough preliminary calculation yields an ionization potential of 12 + volts in satisfactory agreement with the value 13.5 volts, computed by Born.

HARVARD UNIVERSITY,
CAMBRIDGE, MASS.

THE EFFECT OF CERTAIN DISSOLVED SUBSTANCES ON THE INFRA-RED ABSORPTION OF WATER.

BY J. R. COLLINS.

THE absorption spectrum of aqueous solutions of inorganic compounds were studied quantitatively to determine the effect of the solute on the absorption of the water. The spectrum was studied from 0.8 μ to 2.3 μ, which range includes four absorption bands of water. The procedure consisted of determining the per cent. transmission of a measured thickness of the solution and of a thickness of pure water equivalent to the amount of water in the solution.

[1] W. Colby and C. F. Meyer, Astrophys. Journ., 53, p. 300, May, 1921.

[2] E. S. Imes, Astrophys. Journ., 50, p. 251, 1919.

[3] Foote and Mohler, J. Am. Chem. Soc., 42, p. 1832, Sept., 1920.

[4] M. Born, Verh. d. D. Phys. Ges., 21, p. 679, 1919.

As the absorption bands vary widely in their intensities four different thicknesses of solution and water were used for various parts of the spectral region studied. The per cent. transmission curves of the solution and water were plotted together for comparison.

Two spectrometers in series were used to insure purity of the spectrum. These were of the constant deviation type with glass prisms and lenses. A Coblentz linear thermopile and iron-clad galvanometer were used to measure the radiation. A very careful determination of the transmission of various thicknesses of water was made, errors due to reflection in the absorption cells being eliminated by using the two cells of different thickness. These cells were placed in turn in the beam passing through the spectrometer system and thus was determined the transmission of a layer of water equal in thickness to the difference in thickness of the two cells. The transmission of the solutions was determined by obtaining the ratio of the transmission of the solution to that of an equal thickness of water.

The spectrometer was calibrated by the use of emission spectra of lithium, sodium, and potassium salts volatilized in the arc and the mercury arc. A very careful determination of the absorption of water was made in the region .8 μ to 2.3 μ. The positions of maximum absorption of water were located at .97 μ, 1.20 μ, 1.44 μ and 2.00 μ, the corresponding coefficients of absorption being .448, 1.22, 29.4 and 103. The coefficient of absorption α is defined by the relation

$$J = J_0 e^{-\alpha t}.$$

J = transmitted radiation, J_0 = incident radiation, t = thickness of absorbing layer.

The materials used as solutes were NaCl, $AgNO_3$, NH_4NO_3, $CaCl_2$, $BaCl_2$, $SrCl_2$, $MgCl_2$, $Mg(NO_3)_2$, $Zn(NO_3)$ $ZnSO_4$, $Al_2(SO_4)_3$, Al_2Cl_6, $Al_2(NO_3)_6$, $Na_2S_2O_3$, NaOH, KOH, LiOH. The first three are non-hydrating substances, while the rest are supposed to combine to a greater or less extent with some of the water in which they are dissolved. The results are masked to a certain extent by the absorption of the dissolved substances, but a decrease in the absorption of the solution from that of an equivalent amount of pure water is evidence of a change in the absorption of the water caused by the solute.

No general rule is found for the behavior of the hydrating substances: $ZnSO_4$, $Al_2(SO_4)_3$, LiOH, NaOH, KOH, increased the transmission of the water in all four absorption bands; the other hydrating substances increased the transmission of the water in the absorption band at 1.44 μ but do not affect the transmission of the water at the other absorption bands in any regular manner. The three non-hydrating substances decrease the transmission of the water in the two absorption bands at .97 μ and 1.2 μ, increase the transmission of the water in the absorption band at 1.44 μ, and do not affect the transmission in the same way at the remaining absorption band. Thus every substance studied increased the transmission of the water in the absorption band at 1.44 μ.

H. C. Jones[1] attempts to explain the effect on the basis of the solvate theory. In his explanation the transmission of the water should be increased in all the absorption bands by the hydrating substances, and should be unaffected by the non-hydrating substances. This explanation cannot fit the present results without some serious modifications.

CORNELL UNIVERSITY,
December, 1921.

THE ABSORPTION SPECTRUM OF HYDROGEN CHLORIDE AT 200° K.

BY B. J. SPENCE AND C. HOLLEY.

PLANCK[2] assuming that Bohr's static orbits are not the only possible ones (an assumption compatible with the classical laws of electrodynamics) has made a study of the absorption spectrum due to the rotations of electrical doublets with free axes. He finds as one result of this investigation that maximum absorption should occur at the wave length

$$\lambda \text{ max} = 2\pi c \sqrt{\frac{J}{KT}},$$

where c is a constant, K Planck's constant, J the moment of inertia of the doublet, and T the absolute temperature.

The investigation is an attempt to verify the above formula. The absorption of the diatomic gas hydrogen chloride was studied at room temperature and also at 200° K., just above its liquefaction temperature (− 83° C.) at atmospheric pressure. This gas shows absorption bands beyond 10 μ which are attributed to molecular rotation. It also shows a series of bands in the region of 3.5 μ which according to Bjerrum (Nernst Festschrift, 1912) are due to the combination of the frequencies of the bands beyond 10 μ with that of the vibration of the molecule. In the application of the Planck expression, we have assumed that any variation in absorption beyond 10 μ will make itself evident as a change in the absorption in the region at 3.5 μ. to which we have confined our study. The investigation was carried on by means of an infra-red spectroscope of the fixed arm type, using a plane grating of 2,500 lines per inch, kindly loaned to us by Professor H. M. Randall of the University of Michigan.

It was found that there was a greater general absorption at the low temperature than at room temperature. In addition, it was found that the bands due to the lower rotational frequencies as evidenced in the 3.5 μ region were very much less pronounced, almost disappearing at the low temperature, while those corresponding to the higher frequencies were not diminished in anything like a similar ratio. It was also found that the number of bands observed remained the same, with no shift in their wave-length at the low temperature.

[1] Phys. Zeit., Vol. 15, p. 447, 1914.

[2] Annalen der Physik, 53, 24, 1917.

At the low temperature we expected on the basis of the Planck expression that the bands due to the higher frequencies of rotation would be less pronounced or decreased in a greater ratio than those due to the lower frequencies. The investigation appears not to confirm the Planck expression for the temperature chosen.

NORTHWESTERN UNIVERSITY.

TWO NEW LINES IN THE ALUMINUM SPECTRUM AND THEIR POSSIBLE SERIES RELATIONS.

BY G. D. SHALLENBERGER.

WHEN a high potential vacuum spark, which has been described by Millikan,[1] is applied to Al electrodes, two unidentified lines are obtained in the spectrum of this element. They are at λ 4150.6 and λ 2907.4 respectively. Both are strong, well-defined lines. The one with the longer wave-length has the higher intensity rating. It is of about the second or third order of magnitude, while the shorter line is of about the fourth or fifth, as compared with the other Al lines. The assigned wave-lengths are probably correct to .3 or .4 of an Ångstrom unit. It is hardly possible that these lines are due to impurities; since elements which have lines near these positions have other stronger lines elsewhere which did not appear on our plates and the lines of the elements which are present as impurities are faint.

While these lines are apparently not to be placed in any of the simple series, there are however some interesting numerical relations:

I.

	λ	√	Remarks.
1.	2907.4	34,394.97	A new line
	4150.6	24,092.90	A new line
		10,302.07	Frequency difference
2.	3082.3	32,443.3	$(2, p)-(3, d)$ an arc line
	4513.0	22,158.2	An enhanced line
		10,285.1	Frequency difference

Although the frequency differences between these two pairs are almost equal, it is difficult to see why the arc line λ 3082, which belongs to the first subordinate series, should be linked with the enhanced line λ 4513.

II.

1. The frequency of the line at 4150.6 is closely represented by the equation

$$v = (2, p_2, \pi_2) - B(1) - (3, p_2, \pi_2),$$

$$v = 24{,}066.32 \text{ calculated},$$

$$v = 24{,}092.9 \text{ observed}.$$

[1] Astrophysical Journal, 52, p. 47, 1920.

2. The frequency of the line at 2907.4 is fairly well represented by the equation

$$\nu = (2, p_2, \pi_2) - B(1) - (5, p_2, \pi_2),$$
$$\nu = 34{,}451.4 \text{ calculated},$$
$$\nu = 34{,}395.99 \text{ observed}.$$

The above symbols have the following values as given in Seriengesetze der Linienspektra by Dr. B. Dunz.

$$(2, p_2, \pi_2) = 48{,}279.51,$$
$$B(1) = 8{,}882.19,$$
$$(3, p_2, \pi_2) = 15{,}331.00,$$
$$(5, p_2, \pi_2) = 4{,}945.96.$$

While the agreement between calculated and observed values is not as close as might be desired the similarity in meaning of the two equations is suggestive.

UNIVERSITY OF CHICAGO.

THE ASPHERICAL NUCLEUS THEORY APPLIED TO THE PRINCIPAL SERIES OF HELIUM.

BY LUDWIK SILBERSTEIN.

THE quantum theory of spectrum emission combined with the assumption of a non-spherical, axially symmetrical nucleus, is applied to Fowler's principal series of helium, corresponding to the fixed total quantum number $n' = 3$ and the variable ones $n = 4, 5$, etc. The theoretical 'main' components, *i.e.*, those corresponding to the passage of the electron from a circular-equatorial to a circular-equatorial orbit, are correlated with the strongest components observed by Paschen in the first five groups or members of the series and with the centres of the next two members observed (but not split) originally by Fowler. The two constants appearing in the general formula, the modified Rydberg constant N and the coëfficient of asphericity σ are thus determined. The differences between the calculated and the observed wave-lengths are all within the error limits. The finally adopted values are $\sigma = 9.334 \cdot 10^{-4}$ and $N = 109723.22$. The latter, combined with a previously obtained value of N for hydrogen, gives for the ratio of the mass of the hydrogen atom to that of the electron the value 1817. The fine-structure depending on σ, through the product $N\sigma$, is then investigated and discussed numerically in the case of the first two members of the series, the groups 4686 and 3203. The distribution of the theoretical components shows, especially in the case of the first group, some similarity to Paschen's observations, although there are superabundant theoretical components.

EASTMAN KODAK COMPANY.

A PHYSICAL EXPLANATION OF THE ACTION OF THE NEW SINGING TUBE.

BY CHAS. T. KNIPP AND JAKOB KUNZ.

IN the organ pipe energy is supplied by a stream of air which encourages the vibrations in a one-sided way, so that the vibrating column receives an impulse each time when the air moves upward towards the node in the middle of the pipe, and receives no impulse in the opposite motion. It looks as if a pendulum were kept in oscillation by receiving at one end of its path an impulse always in the same direction. If we would apply the momentum of the air jet at the center of the tube, vibrations of the column would be discouraged.

We can communicate momentum to a vertical open-air column by heating it. If we heat the air in a tube by a wire net placed in the lower half of the tube, we will obtain a uniform current of air upwards. If the air is vibrating then as it is moving inward its vibration is increased by the momentum of the upward stream of air, but not increased by moving downward. When we place the hot wire net in the middle of the tube it will tend to increase the pressure of the gas when it is a minimum, *i.e.*, it will discourage oscillations. The same will happen when we place the hot net above the middle. In order to encourage oscillations we have to add momentum in a position and at a moment such that the pressure in the node increases more than it would do because of the oscillations alone. If we put the hot wire net at the lower end of the tube, *i.e.*, in a loop, the effect will be very small or zero. The transfer of heat will depend upon the temperature of the air in contact with the wire net, being greatest when the temperature is lowest. But the temperature in the loop at the lower end does not vary, therefore, the transfer of heat in this position of the gauze does not give rise to oscillations. It tends only to raise the temperature of the gas uniformly. *Heat must therefore be applied between a loop and a node.*

If we cover the upper end of the tube, with the hot net in the most favorable position, the sound ceases, and if we heat by means of a Bunsen burner the outside at the top, we get no sound. This was considered by Rayleigh[1] as possible. But if we change the cross section of the tube at its middle, making the upper, closed part of larger diameter, then the tube will emit a sound. The pressure in the upper half of the tube will increase, partly because the air is heated, partly because of the condensations of the air in the node on the top. The air will expand and now the expansion in the narrow neck is aided by the air being heated by the wall. Here the oscillations are encouraged because each time when the air is expanding by the oscillation the expansion is increased by the heat. In each cycle the vibrating particle receives one push in the right direction. It is this one-sidedness of the action which encourages the oscillations. Moreover, as the heat here has the tendency to increase the pressure near the node, the oscillations will start very readily. A slight modification of this experiment is the glass blower's bulb with a long open

[1] Theory of Sound, Vol. II., p. 231.

neck below, which emits a sound when heated round about the neck. Instead of making the lower part of the tube narrower, we might have an annular area take the place of the narrow tube. Various other modifications are considered. In all cases, in the organ pipe, in Rijke's experiment (the second case) and in the other tubes, the oscillations of a column of air are maintained by a one-sided addition of momentum at the right moment and in the right place.

These experiments belong to a large variety of phenomena in which a direct motion is transformed into a periodic motion, electrically speaking, where direct current is transformed into an alternating current.

UNIVERSITY OF ILLINOIS,
November, 1921.

THEORY OF ACOUSTIC WAVE FILTERS: THE LIMITING FREQUENCIES OF TRANSMISSION.

BY G. W. STEWART.

IN a former abstract[1] the writer presented the description of an acoustic wave filter and an approximate formula for its cut-off frequency. The theory has been slightly modified and has been extended to include three types of filters.

Definitions.—Using complex notation, *acoustic impedance* is the complex ratio of the pressure difference applied and the rate of change of volume displacement.

If X is the volume displacement, P the difference of pressure applied in a portion of the line, the definitions of the inertance, M, and the capacitance, C, are as follows:

$$\frac{Md^2X}{dt^2} = Pe^{i\omega t}, \qquad \frac{X}{C} = Pe^{i\omega t}.$$

Assumptions.—The chief assumptions are as follows:

Any portion of the system consists of mass and stiffness and hence the volume displacement with a sinusoidal applied difference of pressure can always be expressed by $Ie^{i\omega t}$, wherein I is complex.

The algebraic sum of the volume displacements at any junction is zero.

In the practical construction a short line is equivalent to an inertance and capacitance connected in parallel.

Results.—At least three filters are practicable, the single-band-pass filter, the low-frequency-pass filter and the high-frequency-pass filter. The following are the limiting frequencies of zero attenuation, for all three types:

$$f_1 = \frac{1}{2\pi}\sqrt{\frac{1}{M_2C_2}}, \qquad f = \frac{1}{2\pi}\sqrt{\frac{M_1 + 4M_2}{M_1M_2(4C_1 + C_2)}}.$$

All of these filters have been constructed and found to test out in remarkable agreement with the approximate theory.

STATE UNIVERSITY OF IOWA.

[1] PHYS. REV., March, 1921, p. 382.

DIFFRACTION EFFECTS IN SOUND ABSORPTION MEASUREMENTS.

BY PAUL E. SABINE.

THE familiar equation for the decrease of sound in a room with reflecting walls is

$$At = \log. I.$$

A is the rate of decay, t is the time required for the sound to decrease to minimum audible intensity, and I is the initial intensity in terms of this minimum. The value of A is given by the equation

$$A = \frac{\Sigma a_1 s_1}{s} \cdot \frac{v}{p}.$$

The term $\Sigma a_1 s_1$ has been called the total absorbing power of the room and its contents and is the summation of the products of the areas exposed to the sound by the respective coefficients of absorption. v is the velocity of sound and p is the mean free path between reflections. The absorption coefficients of different materials have been measured by noting the difference in the duration of audible sound from known sources produced by bringing measured areas of these materials into a room whose absorbing power is known.

Recent experiments, under the improved conditions afforded by the Sound Chamber of the Wallace Clement Sabine Laboratory, have shown that the apparent absorbing power per unit area of highly absorbent materials is a function of the area of the sample tested, of its shape, and also of its location relative to other absorbing surfaces, when the dimensions of the sample tested are not great compared with the wave length of the sound. Measurements were made for tones one octave apart from C_2 (128 d.v.) to C_7 (4096 d.v.) with samples ranging from .14 to 10.0 square meters. For the frequency at which the absorption of felt is a maximum, namely 1024 d.v., the absorbing power per unit area decreased with increasing area, the ratio in the extreme cases being approximate 3 to 1. The same effect was observed at other frequencies although the variation was not so great.

Long narrow shapes with an area of 3.3 square meters showed an absorbing power some 50 per cent. greater than an equal area in the form of a square.

By a similar method the passage of sound through rectangular openings, varying in size from .34 to 2.8 square meters and having a constant ratio of dimensions, was measured. The same effect was observed as in the case of absorption by the felt. For example, the relative transmissions of C_4 (512), per unit area through the smallest and the largest openings were in the ratio 11 to 8.

A considerable number of experiments have been made, all of which suggest the phenomenon of diffraction in the passage of sound through small openings, and obviously suggest some qualifications in the definition of sound absorption coefficients.

WALLACE CLEMENT SABINE LABORATORY,
RIVERBANK, GENEVA, ILLINOIS.

Analysis of the Energy Distribution in Speech.

By I. B. Crandall and Donald MacKenzie.

An analysis is made of the energy distribution in average speech, with the assumption that the energy is continuously distributed over a wide frequency range. The speech is received by an electrostatic transmitter whose voltage output, amplified about 3,000 fold, is impressed on the grids of twin single-stage amplifiers. The unmodified output of one of these amplifiers is measured by a thermocouple and is a known function of the total energy received by the transmitter. The output of the other amplifier is limited by a series resonant circuit to a narrow band of frequencies, the energy in this band being measured by a second thermocouple.

The entire range from 75 to 5,000 cycles per second is covered by twenty-three settings of the resonant circuit. It is found that at frequencies higher than 5,000 cycles the energy is so small as to be incapable of measurement with this apparatus.

The procedure followed in the observations is to utter, syllable by syllable, a 50-syllable piece of discourse, maintaining as nearly as possible the normal modulation of the voice as when speaking without interruption. As each syllable is spoken readings are made of thermocouple currents (the couples here function as ballistic galvanometers) for both total output and resonant circuit transmission. Such a series of readings is made at each setting of the resonant circuit. Corrections are applied to the results to take into account the transmitter-amplifier characteristic, the transmission characteristics of the resonant circuit, and the unavoidable variations in total energy incidental to frequent repetition of a given syllable.

Curves are obtained for individual voices (4 male, 2 female) and from these a composite curve is drawn. This curve shows a great concentration of speech energy in the low frequencies, a result which would not be expected from previously published data of other experimenters. In view of the fact that with the present apparatus a practically uniform accuracy is attained throughout the whole frequency range it is believed that the results obtained are indicative of the actual energy distribution.

Research Laboratory of the
American Telephone and Telegraph Company
and Western Electric Company, Inc.

The Separation of the Element Chlorine into Isotopes (Isotopic Atomic Species).

By William D. Harkins and Anson Hayes.

A definite increase in the atomic weight of chlorine, equal to 1.55 parts in one thousand, was obtained by Harkins and Broeker in January, 1920. This seems to be the first separation of isotopes reported for which there is any

definite evidence. In the present investigation an altogether independent separation has been carried out on a larger amount of material, and a number of atomic weight determinations have been made with extreme care upon very carefully purified material. These prove that the separation is an actual one and not due to impurities. In all there have been obtained about 4 grams of chlorine of atomic weight 35.515, ten grams of atomic weight 35.498, and 90 g. of atomic weight 35.494, on the basis of a normal atomic weight of 35.460. In addition to this many kilograms of material of both higher and lower atomic weight than the normal have been collected, but the atomic weights of these samples have not been determined. The experiments thus far have been carried out by the diffusion of hydrogen chloride at atmospheric pressure, but the later diffusions will be conducted at low pressures.

The following table gives the increase in atomic weight which should be obtained by diffusion provided the Rayleigh theory holds. The cut gives the number of grams of the substance which must be taken in order to give one gram of product provided the process has an efficiency of 100%.

Cut.	Increase of Atomic Weight.	
	HCl.	Neon.
10	0.021	0.020
100	0.044	0.042
1000	0.067	0.065
10000	0.091	0.091
100000	0.116	0.120
1000000	0.142	0.151
10000000	0.169	0.182

It will be seen that the increase in atomic weight is very nearly a constant times the logarithm of the cut.

UNIVERSITY OF CHICAGO.

ON THE DETERMINATION OF SURFACE THERMAL CONDUCTIVITIES.

BY LETHA A. SMITH.

IT is well known that when heat is transferred through a gas between vertical plane solid boundaries the circuit can be considered to consist of the plates, the this regions of relatively stagnant gas at the surfaces of the plates, and the main body of the gas between these partially stagnant portions. In considering the total equivalent conductivity of this, and of many other arrangements, we find that these partially stagnant surface regions frequently play the most prominent part.

The apparatus which is being used for the study of the equivalent conductivity of these regions consists primarily of six parallel plates of glass or metal, which are separated by insulating frames of wood and rubber. These are

clamped together and give a convenient water-tight apparatus. Each of the five compartments can be continually supplied with water or air by means of tubes let into the frames; and opening are provided for inserting thermometers, thermocouples and stirrers.

The central compartment is filled with hot water, the two outer compartments with flowing cold water at a constant temperature, and the two intermediate compartments with air, these air spaces being the ones across which the conductivity is to be measured. The rate of cooling of the central compartment (and under converse conditions, the rate of warming) is found to give curves of an exponential character, showing that Newton's law of cooling holds over the temperature range investigated. In an apparatus designed in this way, the customary difficulties of a thermal investigation are to a large extent eliminated, and allowances for the comparatively small influence of external conditions can easily be made.

It may be shown that it is possible to calculate the equivalent conductivity of these relatively stagnant regions at the surfaces of the solid boundaries by an analysis (1) of a cooling experiment similar to the one mentioned above, (2) a cooling experiment in which flowing cold water at a constant temperature replaces the air in the first experiment, and (3) a record of temperature gradients as determined by thermocouple measurements. The following values have been obtained for the conductivity of these regions: 33.4×10^{-2} calories per square centimeter per minute per degree Centigrade when the boundary is window glass; and 2.92×10^{-2} to 1.97×10^{-2} calories when the boundary is brass. The latter values depend on the condition of the surface.

McGill University.

The Causes of Reaction Expansions in Amalgams.

By Arthur W. Gray.

This communication offers a simple theory to account for the hitherto unexplained peculiar alternation of contractions and expansions that a dental amalgam undergoes during and after the process of hardening.

The rapid drop to a minimum that forms the first part of the typical curve of reaction expansion evidently represents the end of the stage in which there is predominance of the contraction accompanying solution of the alloy in the mercury and formation of Ag_3Hg_4.

Crystallization of the Ag_3Hg_4 quickly follows its formation. The first minimum in the curve marks the time when the rapidity of the expansion accompanying this crystallization just equals the rapidity of the contraction caused by the simultaneous formation of more Ag_3Hg_4.

As the solution and reaction diminish, the crystallization expansion comes to predominate. This predominance is indicated by the rise of the curve from the first minimum to the first maximum.

The mixing of the alloy with the mercury, whether by trituration or other-

wise, reduces the alloy to particles of microscopic size. Many, if not most, of these particles must, however, be considerably larger than molecules at the time the amalgam is molded into a test specimen.

Consequently, there will be a gradual inward diffusion of the free mercury coating the alloy particles, resulting in still more solution, reaction, and crystallization, which may continue long after the amalgam has begun to harden. The volume changes resulting from this diffusion might easily account for the slow descent of the typical reaction expansion curve after reaching the first maximum, and the very much slower rise that follows.

The gradual changes in shape that the reaction expansion curve can be made to undergo by systematic variation of influencing conditions are exactly what might be reasonably expected if the foregoing hypothesis is correct. Illustrations of such changes are given elsewhere.[1]

CAULK PHYSICAL RESEARCH LABORATORY,
MILFORD, DELAWARE,
December 12, 1921.

THE POROUS PLUG COEFFICIENT FOR AIR.

BY J. R. ROEBUCK.

WORK has been in progress intermittently for some years in this laboratory on the Joule-Thompson effect. Papers have been published on a form of plug[2] and on work with water leading to the mechanical equivalent.[3] Sufficient progress in the problem with air has been made that the accumulation of thoroughly reliable data appears to be only a matter of considerable labor. The initial temperature is controlled by passing the air through a pipe immersed in a fluid which also surrounds the plug chamber, and whose temperature is controlled by an electrical resistance thermostat with coils of pure nickel wire or of manganin. The initial pressure is controlled by a rotating piston regulator whose excursions control a spill valve. The radial form of porous plug is used (l.c., 1). In the pressure range 45–200 atoms, the mass flow past the low pressure thermometer inside the plug can be made large without the kinetic energy of flow becoming appreciable. Data in this field can be duplicated readily with different plugs and different rates of flow. Curves have been obtained for initial temperatures of 25, 50, 75, and 100° C. They are markedly curved, convex toward the temperature axis. Both slope and curvature fall off rapidly from low to high temperature, so that apparently the coefficient will go to zero at about the same temperature (225° by extrapolation) for the whole pressure range.

For the pressure range 1–45 atmospheres, the increased volume of the air

[1] A. W. Gray, Contractions and Expansions of Amalgams with Time, PHYS. REV., *18*, 108–113, 1921. Also, Metallographic Phenomena Observed in Amalgams, Am. Inst. Min. and Met. Eng. Trans., *60*, 678–697, 1919; Journ. National Dental Assn., *6*, 909–925, 1919.

[2] Burnett & Roebuck, Plugs, Rev., 30, 529, 1920.

[3] Physics Rev. (2), II, 79, 1913.

passing the low-pressure thermometer leads quickly to either a markedly increased coefficient which increase depends on the rate of flow and is therefore due to kinetic energy effects; or to such a small heat capacity passing the plug that the errors due to heat gain and which are determined largely by the difference of temperature, become larger than desirable. Warming curves of the plug with the flow stopped may be used to get the maximum value of these corrections. Data have been obtained with the low side pressure appoaching one atmosphere where the values of the coefficient were independent of rate of flow.

Great difficulty has been experienced in obtaining suitable porosity. The plugs used are made of porous porcelain and the porosity reduced to that desired by precipitating barium sulphate within the wall. Unfortunately the precipitate blows out. Repeated fillings lead to very non-uniform porosity and consequently erratic values for the coefficient.

Apparatus is at hand for covering the temperature range + 250° C. to about − 100° C., and the pressure range 1–200 atmospheres. It will be extended to other gases when the air data are completed.

University of Wisconsin,
December 10, 1921.

Ether-drift Experiments at Mount Wilson Solar Observatory.

By Dayton C. Miller.

The ether-drift interferometer with a light-path of 224 feet, which was used by Morley and Miller in the Cleveland experiments of 1904 and 1905,[1] has been remounted at the Mount Wilson Observatory in southern California, and observations were obtained in April and in December, 1921. In some of the earlier observations made on a slightly elevated location there was a small displacement of the interference fringes such as would be expected from a true ether-drift. The present series of observations had the object of determining whether this displacement would be larger at the elevation of about 5,900 feet above sea level, and whether it would be affected by the change in the direction of the earth's motion in space from April to November. It was further decided to determine whether the effect was due to magnetic disturbances, by using a steel base for the optical parts in April, and a concrete base in December.

The results show a definite displacement, periodic in each half revolution of the interferometer, of the kind to be expected, but having an amplitude of one tenth of the presumed amount. This is slightly larger than the displacement obtained in Cleveland in 1905. However, this displacement is always accompanied by a disturbance, periodic in one complete revolution of the interferometer, the cause of which is so far unexplained. Final conclusions cannot be drawn until this disturbing factor has been eliminated, by further

[1] Philosophical Magazine, May, 1905.

experimentation. The observations show that the effect is not due to magnetism, and that its magnitude is about the same in April and December.

CASE SCHOOL OF APPLIED SCIENCE,
CLEVELAND, OHIO,
December 20, 1921.

PHOTO-ELASTICITY OR OPTICAL INVESTIGATION OF STRESS DISTRIBUTION IN SOLID BODIES.

BY PAUL HEYMANS.

THE object of the mathematical theory of elasticity is the analytical determination of the elements defining the elastic state at any point of a solid body, *i.e.*, the directions and the algebraic values of the principal stresses.

The number of cases for which a complete mathematical solution exists is limited and the calculations usually worked out in practice for the computation of stability are in general an adaptation, with simplifying assumptions of sometimes doubtful accuracy, of the ideal and incomplete theoretical solution to the needs of engineering practice.

The photo-elastic methods,[1] lead to the experimental determination of the stress distribution for all two-dimensional elastic problems, provided the material in use is isotropic and obeys Hooke's law of linear proportionality between strain and stress.

Those methods are based upon the temporary birefracting properties shown by transparent bodies, namely by xylonite, when put under stress. By means of: (1) *plane polarized light*, the isoclinic lines from which the lines of principal stress, *i.e.*, *the directions*, (2) *circular polarized light, the values of the difference*, (3) *a lateral extensometer, the values of the sum of the principal stresses are determined* at each point of the body under examination.

As in the two-dimensional elastic problems the stress distribution is independent of the elastic constants, *i.e.*, of the nature of the substance, the stress distribution within the elastic limit is the same for any isotropic substance, xylonite, steel, or others, obeying Hooke's law.

Those methods become of valuable help for the development of general mathematical solutions of elastic problems and also for the direct investigation of specific engineering problems. It is desirable that they be extended to the three-dimensional problems.

The theoretical development of photo-elasticity is in the field of physics; their application chiefly interests the engineer. The author therefore brought their description before the Am. Phys. Soc. and in an address to the Eng. Section of the A. A. A. S. he afterwards considered the application of photo-elasticity to engineering problems.

[1] The development of the photo-elastic methods is largely due to Dr. E. G. Coker, Univ. of London, with whom the author of the paper collaborated in recent research in that line.

Experiments on the Sign of the Electric Charge Assumed by a Metal Immersed in a Liquid.

By Richard D. Kleeman and William Fredrickson.

A knowledge of the sign of the electric charge assumed by a metal plate immersed in a liquid or solution is of importance in the theory of the e.m.f. of a cell and in connection with other subjects. Information about this point may be obtained from the motion of metal particles in colloidal solution under the influence of an electric field. But this method suffers from the disadvantage that the process of getting the particles into colloidal solution may change, and in most cases does change, the surface of the metal particles through the formation of oxides, hydroxides, etc., which might have the effect of changing the sign of the electric charge on the particles. The information obtained from difference of potential and electro-capillary measurements, in the cases where they can be applied, is rendered somewhat untrustworthy on account of the hypotheses underlying the interpretation of the experimental results. A set of experiments was accordingly undertaken which should give trustworthy results, and in which it was made certain that the metal surfaces initially were clean.

Fine wires of different metals were in succession suspended in a liquid by means of a fiber about two meters long, a current sent through the liquid, and the direction of the deflection of the wire noted through a microscope. The wires were carefully cleaned by means of fine sandpaper before being used. In this manner it was found that the metals Cu, W, Ag, Mo, Mg, Al, C, Ni, Au, Pt, Sn, Zn, immersed in distilled water assume a negative charge, or move in the opposite direction the current is flowing, while the metals Bi, Pb, Fe, Cd, assume a positive charge. The metals Bi, Pb, Fe, Au, Pt, Ag, have been obtained in colloidal solution in water and their motion under an electric field measured, which indicates that the metals Au, Pt, Ag, are negatively and the metals Bi, Pb, Fe, positively charged. This falls into line with the preceding results, and in the case of these metals at least the process of getting them into colloidal solution does not affect the sign of their ultimate electric charges.

Union College,
Schenectady, N. Y.

The Analysis of Simple Periodic Curves by a Projection Method with Special References to Estuary Tidal Problems.

By E. V. Henry.

A simple method of projection analysis has been developed which can be applied with great advantage over the customary harmonic analysis to certain special types of periodic curves. It has been used particularly in the case of tidal records for large estuaries such as the river and gulf of St. Lawrence. In the case of estuary tidal analysis by the harmonic methods the Fourier

constants are numerous and arbitrary in character, and they neither correspond individually to separate physical factors nor do they even lead to the expression of any satisfactory empirical relationship between any one tide and any other tide on the same estuary. This makes the analysis for estuary tides fundamentally different from that of ordinary tides where the Fourier constants have a direct physical interpretation with reference to solar and lunar movements.

The apparatus consists of three concentric frames which may be turned in such a manner that an attached graph may be inclined into any plane and the defining angles noted. A beam of light from a suitable illuminating source with a specially chosen lens enables one to obtain a normal parallel beam for projection. A glass plate for recording the projected graph is placed at right angles to the beam.

The theory of the apparatus may be developed from the elements of analytical solid geometry.

The results obtained in the case of estuary tides appear to be most interesting.

1. Any tidal graph for any one of the tidal stations on the St. Lawrence estuary could be projected into any other which was further up the river. Similar projections were possible also in the case of each of the estuaries examined, for example that of Port Essington into that of Port Simpson, in British Columbia; and that of Carter's Beacon into that of Root Creek, in Hudson Bay. In each case only three constants were used. Professor Dayton Miller very kindly arranged to have some of these graphs analyzed by the harmonic method in his laboratory at Cleveland, and it was seen that as many as ten constants were used which varied from tide to tide.

2. It appears probable that a method of prediction for estuary tides, which is sought by hydrographers, may be based on the above relationships. In order to test this the tidal curve at Levis was projected into the curve obtained at Platon, using only two angles. One of these remained the same throughout, whilst the other varied from tide to tide. A graph was plotted with the number of the tide as abscissa and the changing angle as ordinate, the result was a curve which repeated itself every fifty-six tides, and could over a limited range be used for purposes of prediction.

The writer is greatly indebted to Dr. Bell Dawson and to Dr. A. N. Shaw for their keen interest, for the assistance rendered by furnishing the tidal data and for numerous suggestions.

McGILL UNIVERSITY.

A GALVANOMETER METHOD FOR PRODUCING AT A DISTANCE A MAGNIFIED RECORD OF A MECHANICAL MOTION.

BY F. WENNER.

THE purpose of the investigation is the development of a method for producing at a distance a magnified and fairly accurate record of irregular relative

displacements of two elements of a mechanical system. Examples of motions to be recorded are the relative displacement of a horizontal pendulum and its support caused by earthquakes, and the relative displacements of two points on a bridge member caused by transient loads. The method consists essentially in the use of,

(*a*) A coil of insulated wire and a magnet attached respectively to the two parts whose relative motion is to be recorded.

(*b*) A moving coil galvanometer.

(*c*) An inductance connected in parallel with the galvanometer.

(*d*) A pair of insulated conductors or line connecting the coil, whose motion relative to the magnet is to be recorded, and galvanometer.

(*e*) An optical system including the mirror of the galvanometer and a moving photographic film.

The coil and magnet attached to the two parts of the mechanical system whose relative motion is to be recorded are located in what we shall refer to as the originating station. The rest of the apparatus, excepting the line, is located in what we shall refer to as the recording station. The line connects the originating and recording stations.

A relative motion between the coil and magnet in the originating station develops an electromotive force which causes a current in the circuit. This current divides between the inductance and the galvanometer, and that part which passes through the galvanometer causes a torque tending to displace the coil from its equilibrium position.

The optical system produces an image of a line source of light on the moving film and, as it includes the mirror of the galvanometer, gives a record of the motion of the coil of the galvanometer.

With this arrangement the galvanometer has an extra period of vibration which is short in comparison to the period determined by the moment of inertia of the coil and the torsional constant of the suspensions. The vibration in this extra period may be either over damped, critically damped, or under damped, depending upon the relative magnitude of the quantities involved. The conditions giving critical damping and a period of about one tenth of a second may be realized with galvonometers such as have been on the market for a number of years and which have free periods from five to fifteen seconds. By designing the galvanometer especially for this purpose, critical damping with a considerably shorter period should be possible. An important feature of the method is that the sensitivity to those components in the motion to be recorded corresponding in period to the extra period of the galvanometer is only slightly greater than for those components having half this period or several times this period.

The magnification obtainable will depend upon the size of the magnet and the coil used in the originating station, the nature of the apparatus to which the magnet and coil may be attached, the highest frequency component of the motion to be recorded, the accuracy of the record desired, and the resistance

of the line connecting the originating and recording stations. In general, however, the magnification may be as large as desired.

The distance permissible between the originating and recording stations depends to a very large extent upon the same quantities as the magnification. In most cases, however, the distance may be as large as desired up to fifty miles or even more, except in case a high magnification is also desired.

In case of an irregular motion the highest frequency components which may be considered as recorded will depend to a considerable extent upon the accuracy required and pains taken in the design and construction of the apparatus. It should, however, be possible to get a fairly definite idea of the amplitude of the components having frequencies up to fifty cycles per second.

When the coil of the galvanometer is deflected the suspensions exert a torque towards a definite equilibrium position. For this reason very slow motions are not recorded, and this will be a decided advantage in the case of seismometers which are very sensitive to changes in level.

The conclusions stated above were reached mainly from observations of the action of apparatus set up for demonstration purposes, and from calculations made for a single special case. This should therefore be considered as a preliminary report upon the work.

DEPARTMENT OF COMMERCE,
BUREAU OF STANDARDS,
WASHINGTON, D. C.

THE INFLUENCE OF SMALL VARIATIONS IN THE OUTLET OF A SMOOTH BRASS TUBE ON THE DISTRIBUTION OF STATIC PRESSURE WHEN AIR IS FLOWING THROUGH THE TUBE.

BY T. S. TAYLOR.

WHILE measuring the flow of air through a smooth brass tube 150″ long and 7/8″ diameter, it was observed that peculiar variations of the static pressure existed at the outlet. The static pressure for this tube was found to be less than atmospheric at the outlet and it was necessary to move the measuring tube several centimeters back into the brass tube at the center before the static pressure had become atmospheric. As far as could be observed mechanically the tube was smooth, both as to the way it was cut off and as to the existence of bevels or burrs. Results were obtained for different velocities of air, of the distribution of the static pressure for various positions near the outlet and a set of curves obtained, showing the distributions across the tube as well as along the tube. Further microscopic examination of the end of the tube finally revealed an extremely small bevel which was the cause of the disturbances observed. This was undoubtedly there since after taking extreme pains to have the end of the tube smooth and cut off squarely, the static pressure was always atmospheric at the outlet and the distribution was constant across the tube.

A further study was then made to get some ideas relative to the influence of different bevels upon the changes in the static pressure at the outlet. The static pressures were always measured by a carefully constructed static pressure tube made from a small hypodermic needle. A sensitive inclined gage was used to measure the static pressures.

WESTINGHOUSE RESEARCH LABORATORY.

COHESION AND ADHESION.

BY WILSON TAYLOR.

FROM evidence presented in the Philosophical Magazine, June, 1921, pp. 877–889, on "The Coalescence of Liquid Spheres," it is inferred that the force of surface tension is a fundamental property of all free surfaces of mass, acting about the free molecular masses of a gas and causing the molecules to coalesce or cohere in the same way as liquid spheres are observed to do.

Accordingly, measurements were made on mercury spheres suspended freely from the lowest rims of water drops. These spheres ranged in size from .006 mm. to 1.5 mm. in diameter. The vertical lift upon the mercury of the surface tension of the water was compared with the weight of the suspended sphere and it was found that the upward lift was always greater than the weight except when the spheres, on account of their size, were on the point of falling off, and then these two forces were equal. For the smallest sphere the upward lift was seven times the weight.

Again, similar measurements were made on mercury spheres suspended from glass surfaces and ranging from .002 mm. to 2.25 mm. in diameter; and, as before, the vertical lift of the surface tension of the mercury at the line of its attachment to the glass was compared with the weight of the suspended sphere. It was found that the vertical lift as the spheres increased in size gradually decreased from about 13,000 to 2.29 times the weight. Had the surface tension of glass having a value of 239 dynes per cm. been used instead of that of mercury this ratio would have decreased from 6,000 to one of equality as the spheres were on the point of falling off.

Similar evidence in the case of solid bodies suspended from water and of small solid bodies adhering to each other with or without a liquid connecting link showed that as far as could be observed microscopically the same law was in operation.

Also from the evidence referred to above there is reason to think that the law operates as well in the case of molecular masses, that is,

Cohesion and adhesion are simply surface tension forces which exist about all free masses, molecular or larger, attaching themselves to each other in the periphery of the contact area and binding the two masses together in one enveloping surface tension force.

There is thus no evidence of any molecular attraction between the two

masses in the contact area itself but an actual pressure of the one mass upon the other reaching in the case of a water molecule to about 11,000 atmospheres.

UNIVERSITY OF TORONTO,
December 30, 1921.

PROGRESS OF WORK WITH THE CRYSTELLIPTOMETER ON SELENIUM CRYSTALS.

BY LEROY D. WELD.

A CONTINUATION of work treated in a previous paper.[1] The results indicate that fairly consistent data on optical constants can be obtained by reflection even from old crystals of selenium unless accidentally contaminated. There is strong indication of anomalous dispersion, suggesting an absorption band, in the vicinity of wave-length 0.6 micron. Paper will be published immediately in the Journal of the Optical Society.

STATE UNIVERSITY OF IOWA.

THE TRANSMITTED EFFECT IN SELENIUM CRYSTALS.

BY J. C. POMEROY.

LONG needlelike crystals were used, each of which was clamped by electrodes at one or more points.

Measurements were made of the transverse conductivity in the dark and also of the change in this conductivity when a narrow band of light was allowed to fall at the electrodes and at points along the crystal spaced 0.5 mm. apart.

This change of conductivity and its logarithm were plotted against the distance between the electrodes and the spot of light. In general this logarithm was proportional to the distance. In some cases there were marked variations from this rule but these generally could be traced to certain peculiarities in the formation of the crystal.

From the observed facts the writer is led to think that the light effect is transmitted along the crystal by some sort of wave motion. It is hoped that experiments now in progress will throw some further light on this theory.

BETHANY COLLEGE,
WEST VIRGINIA.

FURTHER EXPERIMENTS ON CRITICAL POTENTIALS IN HYDROGEN.

BY F. L. MOHLER, PAUL D. FOOTE, AND E. H. KURTH.

THE discrepancies between previous results of various observers as to the values of critical potentials of hydrogen as well as the differences in interpretations of results led to the following experiments.

A four-electrode tube was constructed with a photo-electric source of electrons instead of the usual thermionic cathode. The arrangement of electrodes

[1] Abstract, N.S., Vol. 11, p. 249, 1918.

and methods of measurement were similar to those used before by two of the authors.[1]

A potassium hydride surface illuminated by an incandescent lamp gave currents ample for measurement of the principle ionization potential and potentials of inelastic impact. Consistent initial potential corrections were obtained from measurement of the potential at which the total current started. The ionization potential thus corrected was 16.0 volts. Inelastic collisions occurred at 10.5 and 22.3 volts.

The photo-electric cathode was replaced by a Wehnelt cathode. The results obtained were practically identical with the above at the same pressures. With higher pressures inelastic impacts occurred at 10.5, 16 and 21 volts. In this respect the results are entirely consistent with the work of Mohler and Foote.

As the above method of applying initial corrections may be questionable, measurements were made with mercury vapor as well as hydrogen in the tube. Pressures were adjusted to give nearly equal amounts of ionization from the two gases and the difference between ionization points was measured. The resulting value for hydrogen is 15.5 volts.

We conclude from the above results that the dissociation of hydrogen by an incandescent wire plays no appreciable part in the phenomena observed. The potentials of inelastic collision at 10.5 and 22.3 indicate resonance potentials at 10.5 and 11.8 volts, due to collisions with normal hydrogen. The possibility that 22.3 volts is a resonance potential and not due to successive impacts is not excluded by this work.

BUREAU OF STANDARDS.

PHOTO-ELECTRIC PHENOMENA IN COATED-FILAMENT AUDION BULBS.

BY R. C. GIBBS AND EDNA L. MEACHAM.

CASE[2] and Merritt[3] have recorded certain observations made upon the photoactive behavior of coated-filament vacuum tubes. Additional experiments intended to examine in more detail some phases of their work have been performed.

With one of the tubes previously used by Merritt, study was mainly made upon the increase in thermionic current that occurs when the coated filament is illuminated. This increase will be referred to as the photo-electric current. For various voltages applied between filament and plate the photo-electric current was found to increase with increase of filament current in very much the same way as the thermionic current. The size of the photo-electric current depended upon the potential of the grid. In order to eliminate a steady drift in thermionic current which was in one direction when the grid was connected to the plate and in the opposite direction when the grid was

[1] Bureau of Standards, Sci. Paper No. 400.

[2] PHYS. REV., Vol. XVII., p. 398, 1921.

[3] PHYS. REV., Vol. XVII., p. 525, 1921.

connected to the filament, a high resistance was connected between filament and plate and the grid connected so as to maintain it at a potential between that of filament and plate. With this connection the photo-electric current reached values as large as 24×10^{-8} amperes for a filament current of 0.9 ampere when it was illuminated by a 400-watt incandescent lamp operated on a storage battery and placed about one foot from the filament of the tube, a narrow slit being interposed to prevent illumination of other parts of the tube. With the grid floating a maximum for the photo-electric current was found for various plate potentials at a filament temperature corresponding to a filament current of about 0.83 ampere. For constant filament current the photo-electric current showed a saturation effect at the higher plate potentials.

It was found that from 8 to 10 minutes were required for the photo-electric current to reach its maximum after turning the illumination on the filament. Furthermore the decay of this current after the illumination was turned off was rather slow. The time of decay varied from 25 to 50 minutes depending upon various conditions of plate potential, filament current, and previous treatment of filament.

The ratio of photo-electric current to thermionic current for the same filament temperature decreased with increase in filament current, with an irregularity that often showed a distinct minimum and maximum between 0.5 and 0.6 ampere in the filament. This irregularity may be due to the fact that the filament was not brought to the same initial condition before the determination of each ratio.

It was early discovered that the ratio just mentioned depended, for a given filament temperature, to a very great extent upon the temperature and light treatment of the filament just previous to its determination.

A long series of observations were made at one filament temperature to determine the effect of this previous temperature and light treatment. At the filament temperature used, that corresponding to a filament current of 0.5 ampere, the ratio of photo-electric current to thermionic current was much larger when the filament had been illuminated at a higher temperature for some time just before. Previous illumination at a lower temperature reduced the ratio. If the filament were not illuminated during these higher and lower temperature treatments the ratio in each case was larger than when illuminated, the difference being more marked for the lower temperature treatment.

CORNELL UNIVERSITY,
August, 1921.

THE INFORMATION SERVICE OF THE NATIONAL RESEARCH COUNCIL.

BY ROBERT M. YERKES.
Chairman, Research Information Service.

THE *clearing-house* for science and technology, established by the National Research Council in 1919, has developed rapidly. It now contains uniquely valuable informational apparatus whose serviceability to investigators will increase as it is perfected and utilized in answering requests.

The Service has specialized on the varieties of informational need which are suggested by the questions who, what, where, and how. Who, refers to the persons engaged in research or qualified for it by training—there are more than 13,000 included in the Personnel File. What, refers to current research, distribution of research interest and activity, problems, published reports of results, bibliographies, bibliographic lists, abstracts, etc. Where, relates to research laboratories and institutes—their construction, equipment, resources and activities. How, concerns methods, processes, technique, apparatus and supplies for research and teaching.

Physicists are urged to acquaint themselves with the organization and functions of the Research Information Service and to avail themselves of its aid. In a multitude of ways it can be made to conserve their time, facilitate and improve their teaching and research. The more the Service is used by those who are actively engaged in the physical, mathematical and biological sciences and their respective branches of engineering, the more valuable it will become.

National Research Council,
Washington, D. C.

Power Factors in Radio Circuits.

By N. H. Williams.

A circuit containing inductance and capacity in series, when used in continuous wave work, is seldom permitted to oscillate at its natural frequency because it is invariably coupled to some other circuit. Hence its power factor may differ widely from unity and the behavior of the system is largely determined by the power factor.

This paper presents a method of measuring the phase relations of two high frequency currents which involves the measurement of each of the two currents, their vector sum, and their vector difference. Two wire loops, each about 20 cm. in diameter, are placed in series and connected to a short constantine ribbon used as a heating element. This element is placed near to a thermal junction and the other junction of this circuit is placed near to a second heating element which is supplied with current from a dry cell. A sensitive galvanometer is used in connection with the thermal junctions. The positions of the two heating elements are adjusted so that they produce equal and opposite effects upon the galvanometer when they both carry the same current.

An auxiliary coil of a few turns is connected into the high frequency circuit. This coil is placed parallel to one of the loops and about 10 cm. from it. There is induced in the loop a current which is proportional to the initial high frequency current. The current from the dry cell is now adjusted to balance the effect of the high frequency current upon the thermal junction and galvanometer and the value of the induced high frequency current is read from the D.-C. ammeter.

A second coil of the same size carrying current of the same frequency may now be placed near the second loop. When the battery current is adjusted to balance the combined effects of the two currents, the ammeter reads their vector sum. By constructing the vector diagram, the phase difference may be measured. The angle thus measured is the complement of the angle whose cosine is the power factor of the oscillatory circuit.

By this means the relations of power factor to frequency, to coupling, and to resistance have been investigated.

UNIVERSITY OF MICHIGAN.

"J" RADIATION: A SUMMARY.

BY F. K. RICHTMYER.

THE frequent reference in the literature of X-rays to the existence of a "J" radiation, of shorter wave-length than the K radiation, seems to warrant a statement summarizing the evidence pro and con, particularly in view of a recent paper by Crowther (Phil. Mag. for November, 1921 (10)).

Previous to that of Crowther, the evidence in favor of the "J" radiation has been based almost entirely on apparent discontinuities in absorption as a function of wave-length. The present writer has shown (8, 9) that, when absorption measurements are made with monochromatic radiation and with a precision of the order of one per cent., these discontinuities disappear.

Crowther bases his evidence for the existence of "J" radiation on the decrease in "hardness" of scattered radiation as compared with the primary beam transmitted at 45° through a thin sheet of aluminum, the scattered beam being measured at 90° from the primary. Since Crowther did not use monochromatic radiation his results (his published data are very meager) can readily be explained by assuming that the scattering coefficient is a function of wave-length.

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CORNELL UNIVERSITY,
December, 1921.

The Dilemma of the Helium Atom.

By John H. Van Vleck.

The study of helium, the simplest atom except hydrogen, should be a key to a generalized Bohr theory of atomic structure. However, no satisfactory model of normal helium has yet been devised, for the models of Bohr, Langmuir, Franck and Reiche, and Landé all give the wrong ionization potentials if the non-radiating orbits are determined by the Sommerfeld quantum conditions.

It therefore seemed desirable to compute the ionization potential of a model suggested by E. C. Kemble,[1] in which the two electrons, I. and II., move in three dimensions with an axial symmetry, so as to have the cylindrical coordinates

$$\text{I. } r, z, \varphi, \qquad \text{II. } r, z, \varphi + \pi.$$

After the dynamical solution was obtained as a power series in a parameter, the constants of integration were determined so as to give the action integral the value demanded by the Sommerfeld quantum conditions, assuming one of the coördinates to be used was the cyclic coördinate φ (giving the system a total angular momentum $h/2\pi$), while the other coördinates were unrestricted, provided they have the period of r and z. The computed ionization potential (74.9 volts) does not agree with the experimental value (79.3 volts), the discrepancy being of the same order as in the Bohr model, which gives an ionizing potential of 82.7 volts.

Since all the simple, symmetrical models of helium, such as are required by its extreme chemical stability, seem to yield impossible ionization potentials, some radical modification of the conventional quantum theory of atomic structure appears necessary. Two such possible modifications are:

1. Reformulation of the quantum conditions. Two very interesting such suggestions have been made by Langmuir.[2] One of these, that the maximum angular momentum of a single electron should equal $h/2\pi$, leads to a correct ionizing potential for his semi-circular dynamical model of helium, but appears contradictory to the fact that in the hydrogen atom and in the theory of rotational specific heats the total angular momentum of the entire system, rather than of a single electron, is $h/2\pi$. Also one would expect this modified quantum condition to be equally applicable to Langmuir's semi-circular hydrogen molecule, almost identical with his helium atom, but computations by the writer indicate that in this case the maximum angular momentum of an electron is not $h/2\pi$, but $.956(h/2\pi)$.

Langmuir's other suggestion, that of a static atom in which the electron is subjected, in addition to the Coulomb force, to a force which it would experience if it were an electrical doublet of strength $1/2em(nh/2\pi)^2$ does not appear to be consistent with the Rutherford scattering experiments, or with the dynamical orbits found in band spectrum theory. Also complicated modifications to the

[1] Phil. Mag., Vol. XLII., p. 132 (July, 1921).

[2] Physical Review, Vol. XVII., p. 349; Vol. XVIII., p. 104.

force would be necessary to account for the Sommerfeld fine-structure or even the shift between the lines of the Balmer hydrogen series and those of the Pickering helium series.

2. Modification of the law of force between negative electrons. The experimental evidence of Rutherford establishes the validity of the inverse square law only between negative electrons and positive nucleii, while Compton concludes that the spiral tracks of beta particles indicate that the field of an electron does not have a spherical symmetry.[1]

HARVARD UNIVERSITY.

MOMENT OF MOMENTUM OF MAGNETIC ELECTRONS.

BY E. H. KENNARD.

ACCORDING to the usual electron theory ferromagnetism is due to the circulation of electrons along paths of considerable length and must therefore be accompanied by mechanical angular momentum equal per unit volume to

$$\Gamma = k\frac{m}{e}I, \tag{1}$$

where I = intensity of magnetization, m/e = ratio of electronic mass and charge in electromagnetic units and k has the value 2. This equation is confirmed as to sign by E. Beck,[2] but he finds $k = 1$ for both iron and nickel. Barnett's results on magnetization by rotation likewise agree as to sign but indicate for k a value decidedly smaller than 2.

A smaller value of k is readily obtained in the theory if we abandon the circulation of electrons as wholes and ascribe ferromagnetism to a rotation of the electron about its own axis.

For instance, suppose a Lorentz electron (uniformly charged sphere) to be set in slow uniform rotation. The resulting external magnetic field is the same as that of a doublet at the center of moment $M = \frac{1}{3}a^2e\omega$, where a = electronic radius and ω = angular speed; hence the density of electromagnetic momentum at any point outside is $g = EH_\theta/4\pi c = eM\sin\theta/4\pi r^5$, where r = distance from center and θ = angle from axis of rotation. Multiplying by $r\sin\theta$ and integrating throughout the space exterior to the electron one finds as the total angular momentum about the axis of rotation $\Gamma = 2eM/3a$. But the mass is, in our units, $2e^2/3a$. Hence $\Gamma = mM/e$ and $k = 1$.

For the ring electron, according to D. L. Webster's theory $k = 2$. But this result is bound up with the essentially speculative foundation of his theory and it seems certain that electrons of the ring type can be made to give other values to k than 2.

CORNELI UNIVERSITY,
December, 1921.

[1] Phil. Mag., Vol. XLI., p. 279, Feb., 1921.
[2] Ann. der Phys., 60, p. 109, 1919.

THEORY OF IONIZATION BY CUMULATIVE ACTION.

BY K. T. COMPTON.

A STUDY of the ionization in a gas subjected to thermionic bombardment between an incandescent cathode and an anode enables certain features of the process of the ionization to be determined. In case of a metallic vapor at more than a couple of millimeters pressure and at moderate voltages, it is readily shown that but a negligible part of the ionization can be due to single direct electronic impacts against atoms. Practically all the ionization is due to ionization of atoms which have previously been partially ionized in the process of producing resonance radiation by a preceding impact or by absorption of such radiation produced by impacts against neighboring molecules.

Under such conditions, and if the thermionic emission is limited by space charge, it is shown that the total number of emitted electrons is:

$$n = \frac{n_0}{1 - 4\sqrt{2}\sqrt{1840 M \pi P_0}},$$

where M is the molecular weight of the gas (on the basis $M_H = 1$), n_0 is the number of electrons which would be emitted under otherwise similar conditions if there were no ionization, P_0 is the probability that any molecule may be in the abnormal or partially ionized condition, and π is a constant which is probably unity for a pure monatomic gas or vapor. By this relation, P_0 may be experimentally determined.

If n_0 be increased, P_0, which increases rapidly with n_0, increases until the thermionic current n would become infinite if it were not limited by the saturation emission at the given temperature. Owing to such limitation, it is shown that the space charge changes sign, with a further increase in current. The maximum arc current cannot exceed two times the saturation value of thermionic emission and, at voltages less than the normal ionizing potential, is probably about one and a half times the thermionic saturation current.

Expressions for P_0 are derived on the assumptions (1) that the abnormal state is the result of a preceding impact against the same molecule and (2) that it results from absorption of resonance radiation. When applied to the particular case of a cathode passing axially inside a cylindrical anode, calculations show that process (2) is much more important than process (1).

This ionization by cumulative action, in which the effect of radiation is very important, is probably of preponderating importance in temperature ionization of gases.

A full report of this work is soon to be published.

PRINCETON UNIVERSITY.

A SIGNIFICANT EXCEPTION TO THE PRINCIPLE OF SELECTION.

BY PAUL D. FOOTE, F. L. MOHLER AND W. F. MEGGERS.

THE pair $1s$–$3d$ of sodium and potassium, in Sommerfeld's theory, necessitates an interorbital transition where the change in azimuthal quantum number is two units. The presence of this pair has been always attributed to the incipient Stark effect of the exciting field. In the present paper an experimental arrangement is described wherein the radiation is completely shielded from the applied field—itself only 7 volts. The pair may then be produced at will by increasing the exciting current until it is one of the strongest lines of the spectrum. It therefore is an exception to the selection principle which can not be explained away by a Stark effect. Its explanation is of deeper origin, possibly requiring a reconsideration of the method whereby single azimuthal quantum numbers have been assigned to each of the s, p, d and b terms.

BUREAU OF STANDARDS.

THE CHARGE ON THE ALPHA PARTICLE.

BY J. E. SHRADER.

THE charge on the alpha particle which is known to consist of two units of electricity has been redetermined by Rutherford and Geiger's method, using the sensitive point and photographic recording apparatus of Geiger.

This method consists essentially of two parts:

1. Measurement of the current due to positive charges from the alpha particles from a given radioactive source.

2. The counting of the alpha particles given off from the same radioactive source.

From the results of these two operations, the charge on the alpha particle and hence the elementary electrical charge has been determined.

Polonium which emits only alpha particles was used as the radioactive source.

The current was determined by the null method with a sensitive quadrant electrometer with an accuracy of about .2 of one per cent.

The counting operation did not give results of comparable accuracy, the error being as great as 4 or 5 per cent. This error is believed to be inherent in the sensitive point method. In operation the sensitive point loses its sensitivity with time and even failure to record is clearly observed. By removal of absorbed gases by electrical heating or by operation of the sensitive point in vacuum, the loss of sensitivity and failure to record are more marked. A failure to record is clearly shown from the fact that the number of particles recorded does not agree with the inverse ratio of the distance and that the number recorded varies with time disproportionate with the rate of decay of the radioactive source.

From observed results, it is believed that the entrance of an alpha particle produces a minute current by ionization by collision and that this stimulates

the release of ionized gas molecules from the point and that this source of ions rather than ionization by collision is responsible for the greater part of the current. Hence the irregularity of counting is due to instability of the gas film.

The value obtained for e by this method taken from an average of several determinations of currents due to positive charges of alpha particles and the number of particles given off from the same source at different rates of counting is 4.78×10^{-10} E.S. units.

The difficulties encountered with the sensitive point method where conditions are hard to control necessarily indicates that this is not a precision method for the determination of e.

WESTINGHOUSE RESEARCH LABORATORY.

RADIATION FROM A GROUP OF ELECTRONS.

BY LEIGH PAGE.

THE most serious contradiction between Bohr's theory of the atom and classical electrodynamics is in connection with the question of radiationless orbits. Bohr's theory requires the existence of such orbits; electrodynamics seems to deny the possibility of them. To be sure, radiation of the first order can be eliminated by assuming that two electrons revolve in a circular orbit at opposite ends of a diameter, but even in the K ring of an atom of atomic number greater than two (helium) the second order radiation from such a pair is greater than the first order radiation from hydrogen. The object of this paper is to investigate the conditions requisite to the annulment of radiation of all orders. That it is possible to devise an atomic structure involving a finite number of electrons which satisfies all of these conditions is extremely doubtful.

Take some point in the atom (the nucleus) as origin. Let $\mathbf{r}$ be the position vector of an electron relative to this origin. Then, by expanding the retarded expression for the electric intensity due to a point charge, the field strength at a great distance R from the origin is found to have the very simple form (in Heaviside-Lorentz rational units),

$$\mathbf{E}_\infty = \frac{1}{4\pi Rc^2}\left\{\left[\frac{d}{dt}(\Sigma e\mathbf{v}) + \frac{1}{c}\frac{d^2}{dt^2}(\Sigma e\mathbf{r}\cdot\mathbf{M}\mathbf{v}) + \frac{1}{2c^2}\frac{d^3}{dt^3}(\Sigma e\overline{\mathbf{r}\cdot\mathbf{M}}^2\mathbf{v}) + \frac{1}{6c^3}\frac{d^4}{dt^4}(\Sigma e\overline{\mathbf{r}\cdot\mathbf{M}}^3\mathbf{v}) + \cdots\right]\times\mathbf{M}\right\}\times\mathbf{M},$$

where $\mathbf{M}$ is a unit vector having the direction of R, and c is the velocity of light. Hence the conditions for radiationless orbits are

1st order:	$\Sigma e\dot{x}_j = \text{const.}$	3 equations,
2d order:	$\Sigma e x_m \dot{x}_j = \text{const.}$	9 equations,
3d order:	$\Sigma e x_m x_n \dot{x}_j = \text{const.}$	18 equations,
4th order:	$\Sigma e x_m x_n x_0 \dot{x}_j = \text{const.}$	30 equations.

where $x_1 \equiv x$, $x_2 \equiv y$, $x_3 \equiv z$, and the subscripts assume the values 1, 2, 3.

As has been pointed out by Professor Sir Joseph Larmor,[1] and as is evident from these equations, a necessary but not sufficient condition for the absence of second order radiation is that the magnetic moment of the atom shall remain constant.

It is easily shown from these conditions that in the case of a circular orbit in which any even number of electrons are uniformly spaced, the odd conditions are all satisfied. If, however, the electrons are limited to two, none of the even conditions are satisfied, the second order radiation amounting to

$$\frac{8}{5}\beta^2\frac{e^2f^2}{\pi c^3}.$$

If there are four electrons in the ring, the second condition is satisfied, but the fourth and higher even conditions are not, and so on. All conditions are satisfied only when a uniform density of charge is distributed around the ring.

A paper containing the details of the work summarized in this abstract is about to be submitted to the PHYSICAL REVIEW for publication.

YALE UNIVERSITY.

A MAGNETIC FALL OF POTENTIAL METHOD FOR TESTING SHORT BARS OF IRON.

BY ARTHUR WHITMORE SMITH.

THE normal magnetization curves (B–H) for bars of iron 6 x 6 mm. in cross section, and 15 cm. in length, have been accurately determined. In testing short bars it is necessary to use a method in which each part of the iron is subjected to equal values of the magnetic intensity, H. This is the case when the iron is in the form of a thin ring, and when test samples can be obtained only as short bars the conditions of a ring circuit (*i.e.*, without ends or air gaps) should be approximated as nearly as possible.

In the present case the test bar is clamped into a yoke of slightly larger section, which carries the flux out one end of the bar and around to the other end. There are two magnetizing coils. One coil is wound over the yoke, and the other coil is around the bar. Each coil carries a current which can be varied without changing the current in the other coil. When these currents are adjusted so that each coil supplies the magnetomotive force needed to carry the magnetic flux through its part of the circuit, and no more, there is no leakage of magnetic flux at any point along the circuit, and the disturbance due to the end effect is not present.

The difficulty is in knowing just when this condition has been reached. The case is analogous to an electric circuit in which the applied e.m.f. is distributed along the circuit with just enough e.m.f. in each element of resistance to keep the current flowing in that element. All of the points in such a circuit will be at the same potential, although a current is flowing, and a voltmeter joined in parallel with a portion of the circuit will indicate no difference of potential.

[1] Phil. Mag., 42, 595, 1921.

The arrangement that corresponds to a voltmeter consists of a solenoid of many turns of fine wire wound on a fiber core 10 cm. in length. Each end of this solenoid is covered with a plate of soft iron, which extends, on one side, about 5 cm. beyond the side of the coil. These plates are clamped against the test bar at points about 10 cm. apart. The solenoid, with its end plates, thus forms a magnetic shunt in parallel with the middle 10 cm. of the bar. The turns of wire around the bar that are displaced by the plates are wound as near as possible to their proper location to give a uniform winding. The flux through the solenoid is measured with a fluxmeter-galvanometer by the usual method of reversals. No flux through the solenoid indicates that the m.m.f. supplied to the bar is just sufficient to carry the flux through the bar.

This apparatus was used with a bar of ingot iron which had been annealed from 1000° C. in a stream of hydrogen. A ring of the same iron, annealed as nearly as possible in the same way, was also measured for a comparison check. The magnetization curves for the ring and for the bar are practically identical, the small differences being less than might be expected from two rings of the same iron. The agreement is equally good for the smaller values of the flux, where other methods require large corrections.

UNIVERSITY OF MICHIGAN,
December 10, 1921.
Revised January 12, 1922.

A NEW METHOD FOR THE DETERMINATION OF THE MAGNETIC SUSCEPTIBILITIES OF GASES.

BY JAKOB KUNZ AND E. C. FRITTS.

IT has been shown by A. P. Carman and W. Hyslop[1] and by R. Whiddington[2] that the thermionic valve in the heterodyne method of electric oscillations gives an exceedingly sensitive and accurate method for the determination of capacities and dielectric constants. The same method is now applied for the measurement of magnetic susceptibilities of gases. In this case the self-induction of a soil in a vacuum is changed by the introduction of the gas, whose susceptibility has to be measured. We hope to measure in this way not only the magnetic susceptibilities of the ordinary and noble gases, but even of metal vapors and of dissociated gases.

UNIVERSITY OF ILLINOIS.

A SINE GALVANOMETER FOR DETERMINING IN ABSOLUTE MEASURE THE HORIZONTAL INTENSITY OF THE EARTH'S MAGNETIC FIELD.

BY S. J. BARNETT.

A BRIEF historical statement with reference to the measurement of the horizontal intensity of the earth's magnetic field by magnetic and electrical

[1] PHYSICAL REVIEW, 15, p. 243, 1920.
[2] Phil. Mag., 40, p. 634, 1920.

methods is followed by a short discussion of sine and tangent galvanometers, which are the chief instruments used in the electrical methods chosen as simplest and otherwise best.

An improvement in the tangent galvanometer is suggested, but the sine galvanometer is considered preferable, though either one can be constructed in such a way as to satisfy the necessary requirements of speed and precision.

An account is given of earlier sine galvanometers designed for absolute measurements, and a detailed description is given of a new instrument designed by the author and constructed under his supervision on strictly modern lines.

The base of the instrument, including tripod, rough and precision circles, microscopes, etc., was taken from a fine European theodolite and made usable by the substitution of non-magnetic parts for parts too magnetic, and further greatly improved by the substitution of electrical illumination of the precision circle for daylight illumination by mirrors.

The magnetometer-box is of pure copper, the damping being chiefly electromagnetic. The magnet-mirror is a fine disc of chrome steel with optically flat and parallel surfaces, being in fact one of the gages made by the Bureau of Standards. The torsion tube and head are similar to those of the C.I.W. magnetometers. A suspension of phosphor bronze strip with torsional constant about 0.001 is generally used. The telescope is small but powerful; the scale is ruled to thirds of mm., on white pyralin. The period of the magnet and the damping, which is adjustable, are such that readings require only a few seconds.

The coil is double, the arrangement being approximately that due to Helmholtz. The spool was machined from white Carrara marble impregnated with paraffin at a temperature near its boiling point—a process insuring high insulation as well as reversibility of thermal changes. The coils were wound, as suggested by J. V. Jones, under tension in a single layer in spiral grooves, which were cut with a diamond tool. The wire is pure copper, especially prepared by the Research Laboratory of the General Electric Company. Each coil is wound in two halves, as suggested by Ayrton, and contains 10 turns with a diameter of approximately 30 cm. and a pitch of approximately 2 mm. The two halves start from the same horizontal plane 180° apart, so that the distance between centers of adjacent wires is approximately 1 mm. The axial distance between the centers of the two coils, or the distance between corresponding turns of the spirals, is approximately 15 cm. The terminals are so constructed as to have negligible magnetic effects at the center of the coils. The leads are small cylindrical cables with coaxial conductors.

The methods of measuring the diameters and axial distances of the spirals are described and the results are given in tables and curves.

The magnetic tests, of three kinds, proving the materials of construction to be satisfactory, are also described.

The theory of the instrument, the methods of adjusting and using it, and the calculation of the error in the constant of the coils arising from imperfections

of construction, as well as of the other errors introduced in the measurement of the horizontal intensity, are given in sufficient detail.

It is shown that the errors in reading the circle and the scale, when sufficiently large angles are used, and the error in the constant of the coil are quite negligible; and that the only other error necessary to consider, viz., that introduced in the measurement of the current traversing the coils, can also be made entirely negligible. In consequence the horizontal intensity of the earth's magnetic field can be determined with an error less than 1 part in 10,000, which is the precision desired, while the magneticians consider 1 part in 5,000 adequate.

With this instrument it is possible to make several complete determinations of the horizontal intensity in one minute; while at least from half an hour to an hour is required with the magnetometer method.

In addition to the preliminary experimental tests, two considerable series of simultaneous determinations of the horizontal intensity have been made with the sine galvanometer and a standard C.I.W. magnetometer by Messrs. Fleming, Fisk, Peters, Ives, and the author. The intensity variations determined from the galvanometer readings have also been compared with those obtained from simultaneous magnetograms of the Cheltenham Observatory. An account of this work will be published shortly by others. The intensities as determined by the different instruments agreed within 1 part in 25,000, though the errors of the electrical standards used, are not known with a precision such as to justify the expectation of an agreement much beyond one part in 4,000 between the absolute value, even if it were not for the limitations of the magnetometer method.

The complete paper will appear shortly in the *Researches* of this Department.

Department of Terrestrial Magnetism,
Carnegie Institution of Washington.

Results of Comparisons of Instruments for Measuring the Earth's Magnetic Elements.

By Louis A. Bauer and J. A. Fleming.

During the period 1905 to 1921 the Department of Terrestrial Magnetism of the Carnegie Institution of Washington has had the opportunity to carry out intercomparisons of magnetic instruments all over the globe. These intercomparisons have been made at the chief magnetic observatories and at various stations of the Department of Terrestrial Magnetism. Thus the intercomparisons apply not alone to the magnetic instruments as designed and constructed by the Department of Terrestrial Magnetism, but also to magnetic instruments of various designs in use by the chief magnetic services. The resulting data besides yielding the information required for the correlation and reduction of magnetic observations made by existing organizations, have likewise yielded results having important bearings upon the principles and methods of magnetic measurements.

One of the most interesting series of such comparisons was that made recently at the standardizing observatory of the Department of Terrestrial Magnetism between our previously adopted standard magnetometer and a sine galvanometer, designed by Dr. Barnett and constructed in the workshop of the Department. With the latter instrument the value of the horizontal intensity of the earth's magnetic field is determined by an electric method, whereas with the standard magnetometer the same magnetic element is obtained by the usual magnetic method. The results of the comparisons between the two instruments showed satisfactory agreement in the values of the horizontal intensity obtained by the two independent methods.

CARNEGIE INSTITUTION.

FURTHER RESULTS OF LINE INTEGRALS OF THE EARTH'S MAGNETIC FORCE.

BY LOUIS A. BAUER AND W. J. PETERS.

A PAPER was presented by the first author at the joint Chicago meeting of Section B of the American Association for the Advancement of Science and the American Physical Society, on December 30, 1920, giving results respecting possible vertical electric currents cutting the earth's surface. The results were obtained on the basis of the magnetic data accumulated by the Department of Terrestrial Magnetism of the Carnegie Institution of Washington.

The present paper gives additional results as derived from recent computations of line integrals around circuits formed by the tracks of the magnetic-survey vessel, the "Carnegie," and the trips of land expeditions sent out by the Department of Terrestrial Magnetism.

One of the most interesting circuits was that formed by Cruise III of the "Carnegie" in the North Atlantic Ocean, in 1914 extending from New York to 80° north, off the northwest coast of Spitzbergen. This circuit embraces an area of 4,441,176 square kilometers. The result of the line integral around this circuit was such as would be produced by currents of positive electricity passing through the air perpendicularly through the earth's surface of average strength one twentieth of an ampere per square kilometer. For the sake of comparison it may be recalled that the line integral around the United States, as based upon the most recent magnetic data, gives a result which could be produced by currents of positive electricity passing from the air perpendicularly through the earth's surface, having an average strength of about one-thirtieth of an ampere per square kilometer.

From the foregoing it is seen that the results of two line integrals, one over an ocean area exclusively, and the other over a land area exclusively, are of the same sign and are practically of the same magnitude. On the other hand, the vertical currents as disclosed by atmospheric-electric observations, according to present methods over the regions of the two line integrals agree, however, in direction with the results of the magnetic line integrals. Quantitatively, there is a pronounced discordance. The strength of the vertical conduction currents

of atmospheric electricity is only about 1/10,000th of the currents indicated by the magnetic line integrals.

Another circuit for which the line integral has just been computed, is that formed by the track of the "Carnegie's" first cruise made in 1909–10. This circuit encloses an ocean area of 13,050,122 square kilometers and extends from New York to England along the track of ocean travel in latitude about 50 degrees north, thence to Madeira and finally back to New York by way of the sailing routes in latitude 20° north. The result of the line integral around this circuit is the same as that which would be produced by currents of positive electricity passing from the air perpendicularly through the earth's surface and having an average current density of one-twenty-sixth of an ampere per square kilometer. This is practically the same result as was obtained by the evaluation of the line integral around the United States.

CARNEGIE INSTITUTION.

CHARACTERISTIC X-RAYS FROM LIGHT ELEMENTS.

BY A. LL. HUGHES.

THE characteristic x-radiations from the very light elements cannot be studied by the method of crystal analysis, as no crystal is known with spacings between its planes large enough to measure wave-lengths longer than about $\lambda 13$. To detect the characteristic radiations from the elements under examination, the photoelectric effect of the radiation from the element, when bombarded by electrons, was plotted as a function of the energy of the electrons. A break in the curve was taken to indicate the appearance of characteristic radiation and the corresponding wave-length was inferred from the quantum relation. The element (carbon or boron) was at a distance of less than a millimeter from an incandescent cathode which served as a source of electrons. In the same vacuum was a nickel or silver plate upon which the radiation fell giving rise to the photoelectric effect. Four gauzes at suitable potentials served to prevent the transfer of electrons or ions to the plate giving the photoelectric effect. Breaks were found at 215 volts ($\lambda 57.5$) and 34.5 volts ($\lambda 358$) for carbon, and at 148 volts ($\lambda 83.5$) and 24.5 volts ($\lambda 505$) for boron. These are the K and L radiations respectively for the elements investigated.

These values can be compared with the theoretical values obtained on extrapolating, by means of Moseley's relation, the known values for the x-ray wave lengths as given in Duane's "Data relating to x-ray Spectra." On extrapolating the values for the $K\alpha_1$ emission lines (and converting into volts), we obtain 275 volts for carbon and 182 volts for boron, and on extrapolating the values for the Ka critical absorption frequencies we obtain 243 volts for carbon and 149 volts for boron. The method employed in this investigation should give values corresponding to the Ka critical points rather than to the $K\alpha_1$ emission lines. The experimental value for boron (148 volts) is in good agreement with the extrapolated Ka value, while that for carbon (215 volts) is lower than the extrapolated value.

Attention is called to the fact that when the square roots of the frequencies of the $K\alpha_1$ emission lines (extrapolated below sodium), are plotted against atomic numbers, the line obtained crosses the line on which lie the square roots of the corresponding critical absorption frequencies (extrapolated below magnesium), between neon and fluorine. That is to say, for elements with atomic numbers below 10, the $K\alpha_1$ emission line would be of *shorter* wave-length than that corresponding to the Ka critical absorption frequency. This is so contrary to the usual views regarding their relative positions, both on theoretical and experimental grounds, that the justification for extrapolation of one or both of these lines must be questioned. It is significant that the reversal of their usual positions takes place just below neon, *i.e.*, their relative positions are only normal down to the element neon, which is the lightest element in which the K shell of electrons is surrounded by a completed outer shell. It is evident therefore that experimental evidence as to the structure of the K radiations for light elements is much to be desired.

The break at 34.5 volts for carbon, corresponds to $\lambda 358$, which is just below shorter than the shortest of the L emission lines in the spectrum of carbon as found by Millikan, as it should be if it is the L critical absorption point.

QUEEN'S UNIVERSITY,
KINGSTON, ONTARIO.

ENERGY RELATIONS BETWEEN X- AND β-RAYS.

BY J. A. GRAY.

EXPERIMENTS have been carried out with the β-rays of radium E in order to determine the relative amounts of energy in the x-rays formed by these β-rays when they penetrate different materials. Paper, iron and lead were the materials used. In making the determinations, it has been assumed that the energy in a beam of x- or β-rays is proportional to the total ionization produced by the beam in air.

If a beam of β-rays of energy E_1, strikes a plate so thin that an inappreciable number of them is scattered by the plate, and x-rays of energy E_2 are formed in the plate we may write

$$E_2 = \lambda E_1 m,$$

where m = mass per unit area of the plate. The quantity λ may be called the mass transformation coefficient. The following values of it have been found: for carbon it equals 0.047, iron 0.110 and lead 0.300. These numbers are in the proportion 1 : 2.3 : 7.2.

When the β-rays of radium E are completely absorbed by paper 0.4 per cent. of their energy is transformed into energy of x-radiation. The corresponding values for iron and lead are 1.35 per cent. and 6 per cent. respectively. These numbers are in the proportion 1 : 3.4 : 15. It is known that when scattering is taken into account, β-rays can pass through a greater mass of materials of

high atomic weight than of materials of low atomic weight. The numbers given above show this, and indicate that the "mass" range of β-rays is about 15/7.2 times or twice as great in lead as in paper.

From the results it can be shown that, in general, secondary β-rays after their expulsion can only give rise to a negligible proportion of the secondary x- or γ-rays formed when a primary beam of x- or γ-rays pass through matter.

McGill University.

Positive Ray Analysis of Zinc and Calcium.

By A. J. Dempster.

Further experiments with zinc have shown that large variations occur in the proportions of the four components observed.[1] This makes the reasoning invalid in which the atomic weights were deduced to be 63, 65, 67 and 69, in order that the mean weight might agree with the chemical atomic weight 65.4. With calcium anodes to which a little zinc had been added, it was found possible to obtain the calcium and zinc lines at the same time and compare their atomic weights. The zinc lines were thus found to have the atomic weights 64, 66, 68 and 70. This makes zinc agree with the rule observed to hold in the isotopes of the inert gases, that even atomic weight usually goes with even atomic number. The strong calcium line at 40 was compared with a potassium line at 39 and a magnesium line at 24. With calcium a weak component was observed with atomic weight 44. This is provisionally considered to be a real isotope and not due to carbon dioxide, since any calcium carbonate present should be dissociated at a lower temperature than that used.

University of Chicago.

The Effect of Dissolved Substances on the Deposition of Colloidal Particles from a Solution by Means of an Electric Current.

By Richard D. Kleeman.

During some experiments on the electric deposition of porcelain slip it was observed that the closeness of the particles of the deposit obtained was affected by a small quantity of a substance dissolved in the slip, the magnitude of the effect depending on the nature of the substance dissolved. Thus for example, the deposit obtained from a slip containing about 1/300 of its weight of sodium silicate (Na_2SiO_3) is hard though not quite dry, while that obtained without the admixture of sodium silicate is of a semi-liquid consistency like cream. Similar results were obtained with Na_3PO_4, Na_2HPO_4, Na_2SO_4, H tartrate, Na tartrate, NaOH, KOH, and in fact most substances show the same effect in a more or less degree.

The effect was found to be closely associated with the increase in fluidity

[1] Physical Review, (2) xix., p. 271.

of the slip obtained on adding a small quantity of one of these substances. This permits a considerable amount of colloidal matter to be added to the solution with the substance, without a change in the fluidity, the amount of matter added affording a sort of measure of the increase in fluidity introduced by the dissolved substance. The latter effect is known and is used to obtain a concentrated porcelain slip for casting in the wet porcelain process by the addition of a small quantity of sodium silicate. It was found that the increase in compactness of the deposit on adding a small quantity of the foregoing substances was attended by an increase in the fluidity of the solution.

These two effects and their association may be explained by supposing that the dissolved substance decreases the "radii of the spheres of action" of the colloidal particles. The particles would accordingly, on addition of the substance, have additional room for motion with a resultant increase in the fluidity in the solution, and would pack more closely on being deposited by an electric current. A theoretical investigation along these lines is given.

It is evident that if the radii of the spheres of action of the particles are decreased sufficiently spontaneous precipitation would result. Thus it would follow from the foregoing results that a substance which precipitates a colloidal solution, if added in an appropriate amount, should in all cases increase the fluidity of the solution and increase the compactness of the deposit obtained with an electric current.

RESEARCH LABORATORY,
GENERAL ELECTRIC COMPANY,
SCHENECTADY, N. Y.

THE EFFECTIVE RANGE OF β-RAYS.

BY J. A. GRAY AND A. V. DOUGLAS.

WHEN plates of any substance are placed over a source of β-rays, a thickness of the substance will eventually be reached such that none of the original β-rays will pass through it. The smallest mass per unit area of the substance which will satisfy this condition is called the effective range of the β-rays in that substance. It is called effective range owing to the fact that, through scattering, β-rays really have a greater total path than that indicated by these measurements. Mass per unit area is taken instead of thickness so as to compare different substances.

This range has been obtained by using an electroscope to give a measure of the intensity of the β-rays. The source of β-rays was an active preparation of radium (D + E). The effective range of these β-rays has been found in paper, aluminium, copper, tin and lead. In paper the range is 0.47 gramme, in lead 0.34 gramme, the range being inversely proportional to what has been called the mass absorption coefficient of the β-rays.

The range in paper has also been obtained of rays scattered through large angles by sheets of silver and lead. Although the rays examined are slower, on the whole, than the primary rays, there is a strong indication that β-rays

lose only a small proportion of their energy, when they are scattered through large angles. It is difficult to be quite certain that they lose any at all, because the scattering of β-rays is not a surface effect.

The effective ranges of secondary β-rays excited in lead by different types of x- and γ-rays have also been determined and are being found useful in problems connected with the transformation of β-rays into x-rays and vice versa.

McGILL UNIVERSITY.

ON THE HIGH FREQUENCY RAYS IN THE γ-RAY SPECTRUM OF RADIUM B AND C.

BY ALOIS F. KOVARIK.

THE method described was devised for the study of the spectra of soft γ-rays, for example, the γ-rays from radium DE—an investigation which is planned by the writer. However, since the penetrating radiations offer a better chance to test the method and also because the only work on record on the γ-ray spectrum of radium is by the photographic method [1] it was thought advisable to study at first the spectrum of the γ-rays from radium B and C. The work here recorded is preliminary to a study of the whole spectrum and bears on the high frequency radiations alone.

The source of the radiations was a standard radium salt of 1.3 milligrams radium content. The radium was placed in the center of a lead block 15 cm. on the edge and the rays passed through an opening in this block and through a slit 1 mm. wide and 6 cm. deep in another block of lead placed in front of the former. The rays fell on a crystal of calcite and were reflected into a point discharge counting chamber after passing through a slit 0.5 mm. wide and 7 cm. deep placed in front of the counting chamber. The counting chamber was also surrounded by lead. The crystal and the counting chamber were moved together, the latter through double the angle of the former and the discharges produced in the counting chamber by the γ-rays entering through the slit (and otherwise) were automatically registered using the device previously described by the writer.[2]

The principal lines recorded by Rutherford were verified but other lines were also detected. Among these, it is of especial interest to note that there are at least five and possibly more lines of shorter wave-length than the shortest one (43′ from rocksalt) reported by Rutherford and Andrade. The glancing angles from calcite of these lines are 41′ (corresponding to the 43′ from rocksalt), 37.5′, 33′, 27.5′, 21′, and 16′.

The study will be carried on, using crystals of various kinds and also of various thicknesses. The method is applicable in particular to the study of rays from weak sources, as is seen from the present case in which only a little more than a milligram of radium was used.

YALE UNIVERSITY.

[1] Rutherford and Andrade, Phil. Mag., 27, 854; 28, 263, 1914.

[2] Kovarik, PHYS. REV., (2), xviii., 272, 1919.

THE BEGINNING OF THE K AND L SERIES OF X-RAYS.

BY F. L. MOHLER AND PAUL D. FOOTE.

MEASUREMENTS of radiation from a thermionic discharge in gases and vapors have been made by means of its photoelectric effect on electrodes within the same tube but electrically shielded from the discharge. This radiation current is nearly a linear function of the voltage across the arc with changes in slope at the critical potentials. A previous paper[1] gave measurements for some metallic vapors that showed critical potentials due to the softest x-rays of these elements.

Measurements have now been extended to twelve elements and compounds from which can be identified the L limits of five elements in the second row of the periodic table and the K series for four in the first row. The gases and vapors used were BCl_3, CO, CO_2, C_2H_4, CCl_4, Air, O_2, Na, Mg, P, S and K. The last showed M limits given in the above-mentioned paper.

The L limits can be identified by the agreement with values computed from the observed K spectra. We find not only the principal L limit

$$La_{1,2} = Ka - K\alpha_{1,2}$$

but potentials corresponding to the hitherto unknown limits,

$$La_{5,6} = Ka - K\alpha_{5,6}$$

and in one or two cases

$$La_{3,4} = Ka - K\alpha_{3,4}.$$

Element.	Z.	Observed Potentials Volts.	K Limits λ in A.	L Limits Observed λ in A.	L Limits Computed λ in A.
Boron	5	186	66.4		
		125			
Carbon	6	272	45.4		
		234			
Nitrogen	7	374	33.0		
		352			
Oxygen	8	478	25.8		
Sodium	11	35		353	
		17		725	
Magnesium	12	46		268	263
		33		374	303 422
Phosphorous	15	126		98	92.2
		110		112	103
		95		130	
Sulphur	16	152		81.2	77.1
		122		101	99.9
Chlorine	17	198		62.3	61.9
		175		70.5	
		157		78.6	

[1] Abs. PHYS. REV., 18, D. 94; 1921.

A plot of the square root of these frequencies against atomic number gives three nearly parallel straight lines.

The potentials ascribed to the K limits likewise give a straight line. It is interesting to note that the ionization potential of He falls on the K line and that of Ne on the principal L line. The table gives only critical potentials that fall in the region of x-ray limits. It must be emphasized that the experimental errors in "computed L limits" are of the same magnitude as for the observed points.

BUREAU OF STANDARDS.

SECONDARY X-RAYS FROM CRYSTALS.

BY G. E. M. JAUNCEY.

USING a Bragg x-ray spectrometer, the crystal was fixed at a certain angle and the ionization chamber was set at a series of angles between an angle $A°$, which was near zero, and 90°. The slit in front of the ionization chamber subtended an angle of 6° at the center of the table, while the angular width of the beam of primary x-rays incident on the crystal was less than 0.25°. Using the general radiation from an x-ray tube with a tungsten target, it was found that, although the maximum deflection of the electrometer occurred when the angle of the ionization chamber was double that of the crystal, yet the deflection was quite appreciable at other angles of the ionization chamber.

From the curve showing the relation between the intensity at various angles and the angle of the ionization chamber, the value I_s of the total intensity of radiation emitted by the crystal between the angles of $A°$ and 90° in the plane of reflection was calculated. The ratio of I_r to I_s, where I_r is the intensity at the position of reflection, is shown in the following table:

Rocksalt Crystal.

Crystal Angle Degrees.	Angle A Degrees.	I_r/I_s Per Cent.
7	7	33
10	10	19
15	15	18

From the table it is seen that the reflected radiation constitutes less than one half of the total radiation emitted by the crystal. There is radiation at all angles up to 90°, the regularly reflected radiation being added to that which is radiated at all angles.

Setting the crystal at an angle of 7° and the ionization chamber at 60°, the absorption produced by 3 mm. of aluminium when placed in the primary and then in the secondary beam was determined. In the primary beam the aluminium reduced the intensity to 46 per cent., while in the secondary it

reduced the intensity to 42.5 per cent. There seems, therefore, to be some fluorescent radiation present.

WASHINGTON UNIVERSITY,
ST. LOUIS, MO.,
December 12, 1921.

BRIGHTNESS OF TUNGSTEN.

BY W. E. FORSYTHE.

THE brightness of tungsten in candles per square centimeter has been measured by three different methods for a wide range of temperatures. The first method used was the direct one where the light from a definite length of a filament of a known diameter was measured for a temperature of about 2350° K. and from the values thus obtained the brightness per square centimeter calculated. Values were thus obtained using special 20-mil. tungsten lamps and also special lamps with a ribbon filament several centimeters long, 2 mm. wide and about .01 mm. thick. Values of the brightness for points a few hundred degrees above and below this were obtained in terms of this value by direct comparison. By this method the brightness was measured from 2080° K. to 2600° K.

The second method was to use as a brightness photometer a disappearing filament optical pyrometer having for the monochromatic screen a yellow-green glass whose effective wave-length for the different temperature intervals was very close to the Crova wave-length for the same temperature intervals. This pyrometer was calibrated for brightness from a black body. Since both the Crova wave-length and the effective wave-length of the screen used, as well as the different temperature intervals over which measurements were made were known, it was possible to correct values of brightness obtained to the values that would have been obtained if the Crova wave-length had been used in each case. By this method the brightness was measured from about 1000° K. to about 3400° K.

The third method was by calculation using the following relation involving the brightness of the black body, the color temperature (Tc) and brightness temperature (S) of the tungsten.

$$B_w = B_{BB} \cdot \frac{e^{-\frac{c_2}{\lambda S}}}{e^{-\frac{c_2}{\lambda Tc}}},$$

where B_{BB} is the brightness of a black body at a temperature $T = Tc$. By this method values were obtained for a temperature range from about 1000° K. to the melting point of tungsten. The three methods gave results that agreed well within the experimental error. The values obtained were plotted log B_w against log T and from the smooth curve the values given in the table were obtained.

The true temperatures (T) of the tungsten used were calculated from the brightness temperatures and the emissive powers given by Worthing.[1] The values of the brightness given in the table are on the scale of candle-power adopted by the Bureau of Standards. The values of the brightness given agree well with those given by Langmuir[2] when the difference in the temperature scale is taken into account and account is taken of the fact that Langmuir's values are not on this scale of candle-power. From the smooth curve between log B and log T the change in brightness due to a change in temperature was obtained for the different temperatures and the values given in the third column of the table. As might be expected these values of the relative change are about the same as are obtained from the black body.

TABLE I.

Brightness and Variation in Brightness at Various Temperatures.

Temperature °K.	Brightness Candles per Square Centimeter.	Per Cent. Change in Candle-power for One Per Cent. Change in Temperature.
1000	.000098	27.0
1200	.00585	21.6
1400	.1075	18.1
1600	.925	15.6
1800	5.21	13.7
2000	20.1	12.3
2200	61.7	11.2
2400	155.5	10.3
2600	343	9.5
2800	679	8.9
3000	1235	8.4
3200	2105	8.1
3400	3380	7.9
3600	5200	7.8

NELA RESEARCH LABORATORY OF PURE SCIENCE,
CLEVELAND, OHIO.

THE LUMINESCENCE OF SOLIDIFYING ANTIMONY.

BY E. KARRER.

WHEN antimony is heated to a temperature above its melting point (630° C.) it becomes bright red. If it is then allowed to cool, its brightness will decrease with the temperature down to the point where solidification sets in, where a sudden increase in brightness occurs. The temperature also increases at this point. The phenomenon is therefore very similar to recalescence in iron. The brightness after the flash appears greater for a given temperature than the brightness at the same temperature before the flash. Thus it appears from this fact to be a case of crystal-luminescence.

[1] PHYSICAL REVIEW, (2), x., p. 389, 1917.

[2] PHYSICAL REVIEW, (2), vii., p. 302, 1916.

The phenomenon is not due to the oxidation of the antimony since it takes place in hydrogen and in vacuum.

One sample of bismuth showed the same phenomenon occurring at the same temperature. This was due to contamination of the bismuth. Roughly one part of antimony in 2,000 of bismuth is sufficient to show luminescence.

Details will appear in Journal Am. Opt. Soc.

NELA RESEARCH LABORATORIES,
CLEVELAND, OHIO,
December, 1921.

THE THERMIONIC WORK FUNCTION OF TUNGSTEN.

BY C. DAVISSON AND L. H. GERMER.

IN the derivation of Richardson's equation, $i = AT^{1/2}\epsilon^{-b/T}$, the constant b is related to the energy, Φe, required to liberate a single electron through the equation, $\Phi e = bk$, where k is Boltzmann's gas constant and e the electronic charge. Φ is referred to as the equivalent voltage of the work function.

The authors have made a direct calorimetric determination of Φ upon a filament of pure tungsten by the measurement of changes arising from the cooling effect of the emission. At the same time the b of Richardson's equation has been determined, and the calorimetric Φ has been compared with bk/e. With the exception of some work done on oxide-coated platinum filaments by W. Wilson[1] this is the first measurement of these two constants ever made upon the same filament.

The value of Φ has been computed from the relation,

$$\Phi = \frac{2EI}{E - I\frac{dE}{dI}} \cdot \frac{\Delta E}{i},$$

where ΔE is the change in voltage across the filament caused by the emission, i, while the heating current, I, is maintained constant. All essential measurements were made upon a Leeds and Northup potentiometer. After correcting for several spurious effects our final value is

$$\Phi = 4.91 \pm .05 \text{ volt.}$$

For the determination of b the temperatures of the filament must be accurately known. The calculation of these temperatures has been based on the temperature characteristics of tungsten published by Langmuir and by Worthing and Forsythe. Langmuir's data lead to a value of b equal to 5.646×10^4 degrees, while those of Worthing and Forsythe lead to the value 5.541×10^4 degrees. The relation between resistivity and power radiated per unit area for the filament used in the present experiment was found to be accurately consistent with Worthing and Forsythe's data. Furthermore, the temperature scale of Worthing and Forsythe is probably more accurate than the scale of

[1] Nat. Acad. of Sci. Proc., 3, p. 426 (1917).

Langmuir. From both of these considerations it is believed that the latter value of b is the more reliable.

The derivation of Richardson's equation, with the assumptions involved, requires that the values of Φ and of bk/e for a given material be identical. The values of b given above correspond to values of bk/e that are, respectively, 0.8 per cent. and 2.7 per cent. lower than the calorimetrically determined Φ. Since the value of b, corresponding to the greater of these discrepancies is regarded as the more reliable, a real, though small, difference between the constants is indicated. There is some question, however, as to what probable error should be assigned to the values of b. For this reason we do not feel that a difference between Φ and bk/e can be regarded as definitely established.

RESEARCH LABORATORIES OF THE
AMERICAN TELEPHONE AND TELEGRAPH COMPANY
AND THE WESTERN ELECTRIC COMPANY, INC.

A SPECTROSCOPIC METHOD FOR DETERMINING THE EFFECTIVE TEMPERATURE OF ABSORBING AND EMITTING MOLECULES.

BY RAYMOND T. BIRGE.

IN a preliminary investigation[1] of the distribution of intensity in typical band series, as affected by temperature, it was found that Kemble's formula for the statistical distribution of angular velocities did not exactly represent the intensity distribution. This is to be expected, since the intensity, on the quantum theory of band spectra,[2] should be given by $I = (E - E')B_{m'}{}^{m}(a_m)$. If this expression refers to absorption spectra, then, labeling the missing line $m = 0$, the value of m for any line refers to the number of quanta of angular momentum in the initial state.[3] The third factor, $a_{m'}$ then gives the distribution of angular momentum, and if "J" is a constant, the distribution of angular velocities as well. On this assumption Kemble's formula is the theoretical expression for a_m.

Now $E - E' (= h\nu)$ varies only slightly throughout a band. $B_{m'}{}^{m}$, from the author's curves of intensity distribution, varies slowly with m, if m is not too small. The moment of inertia of the molecule in its initial condition (J) can be obtained from the coefficient of the first power term of the Deslandres' formula for the series considered.[4] The deviations of the CN series from a parabolic law show that J is not constant, but that it is approximately so.

The value of m corresponding to maximum intensity, in Kemble's formula, is

$$m_m = \frac{2\pi}{h}\sqrt{kJT},$$

where k is the gas constant per molecule. This connects m with the absolute

[1] PHYS. REV., 18, 319, 1921.
[2] Heurlinger, Zeit. f. Physik, 1, 82, 1920.
[3] Kratzer, Zeit. f. Physik, 3, 289, 1920.
[4] See Sommerfeld's Atombau, 2d edition, p. 555.

temperature of the absorbing or emitting gas, with the approximations mentioned. These approximations are such as to have little effect on the position of m_m, although they decidedly affect the form of other parts of the intensity curve. Introducing the known values for the A series of the 3883 CN band, we have $T = 5.5m^2$.

In active nitrogen,[5] m_m is estimated to be at 9 ± 2. For the 4216 band,[1] for which J is the same, I estimate m_m at $8 \pm 1\frac{1}{2}$. This latter figure gives $T = 80°$ C. $\pm$ 150°. The actual temperature is believed by investigators to be somewhere between room temperature and 100° C. In King's 2700° furnace spectra, m_m should be 23.25,—in the 2500° spectra, 22.45. In each case I find it to be 23 ± 2. (This result has been obtained with far greater care than the preliminary value of 22 previously published.[2])

Assuming then the approximate validity of the formula, we obtain for King's 4 amp. arc a temperature of 4000° C. $\pm$ 300° (from $m_m = 28 \pm 1$), and for my 13 amp. arc 4700° C. $\pm$ 300° (from $m_m = 30 \pm 1$). These values are consistent with previous estimates of the temperature of the arc. A spectrogram taken by King, showing the 3883 band in absorption at about 3000° C. indicates, as nearly as can be judged, that the intensity distribution in absorption is the same as in emission, at the same temperature. Assuming this, an examination of a solar spectrogram lent by Dr. St. John indicates an effective temperature for the CN (or possibly N_2) molecules of the reversing layer of the sun probably hotter than King's arc, and as nearly as can be judged, the *same* as the 13 amp. arc, *i.e.*, 4700° C. This estimate is probably too low, if anything, due to the approximations used. It is believed however that this method can be employed for the quantitative determination of effective solar temperatures.

PHYSICAL LABORATORY,
UNIVERSITY OF CALIFORNIA.

THE EXCITATION OF THE ENHANCED SPECTRA OF SODIUM AND POTASSIUM IN A LOW VOLTAGE ARC.

BY PAUL D. FOOTE, W. F. MEGGERS, AND F. L. MOHLER.

THE enhanced spectrum of sodium and its L-radiation are excited at about the same voltage. Similarly, the M-radiation and the enhanced spectrum of potassium appear simultaneously.

The highest frequency in the simply enhanced spectrum of sodium is estimated to be in the neighborhood of 14 volts and of potassium, 11 volts.

The evidence confirms the theories of Bohr and Sommerfeld which attribute enhanced lines to the ionized atom, and arc lines to the neutral atom.

The following table summarizes the values of the critical voltages characterizing the three-stage development in the spectra of sodium and potassium.

[1] Strutt and Fowler, Proc. Roy. Soc., A86, Plate op. p. 117, 1911.

[2] All the results here quoted were obtained before their quantitative theoretical significance was realized. They are therefore unbiased in this respect.

Element.	Volts.	Notation.	Spectrum.
Sodium.....	2.09	1s–2p	Single pair
	5.11	1s	arc lines,
	35–30	...	enhanced lines and L-radiation $L_\alpha = 35\ L_\alpha$
Potassium.....	1.60	1s–2p	Single pair $= 30$
	4.32	1s	arc lines,
	23	...	enhanced lines and M-radiation.
	20		

Highest frequency in enhanced spectrum: sodium = 14 volts; potassium = 11 volts. Total work of double ionization: sodium = 49 volts: potassium = 34 volts.

BUREAU OF STANDARDS.

THE SIGNIFICANCE OF THE 1/2 TERMS IN SPECTRAL SERIES FORMULÆ.

BY PAUL D. FOOTE AND F. L. MOHLER.

SOMMERFELD showed that the relation between the Ritz series constant a for the arc spectra of the alkalies and a^* for the spark spectra of the alkali earths was of the form $a^*/a = 2$. To verify this for the $m\mathfrak{S}$ and ms terms it was necessary to assign half integral values to m. However, by postulating two rings of electrons, the outer ring containing the generally accepted number of electrons, 8, 18, etc., and considering the shrinkage of the rings when the nuclear charge is increased, the computed ratios a^*/a run from 1.48 to 1.66 and are closely satisfied by $\mathfrak{S}$ and s if to m we assign integral values. The simple physical conceptions of the quantum theory suggest that m should be an integer and in the present paper as good evidence is offered confirming this viewpoint as has been advocated to the contrary.

BUREAU OF STANDARDS.

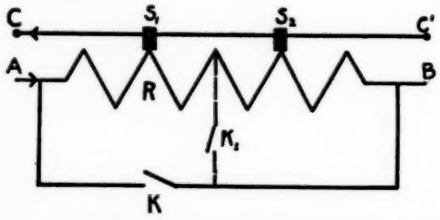
A METHOD FOR INCREASING THE CARRYING CAPACITY OF A RHEOSTAT.

BY W. E. FORSYTHE.

WHEN using an ordinary slide resistance to control a current it often happens that when the current is the largest only a small part of the resistance is being used. This may be disadvantageous for two reasons: In the first place, the smallest change possible in this small part of the resistance may greatly increase the current and in the second place, the resistance may be very much overheated. To overcome these difficulties a method has been devised whereby it is possible to use both ends of the rheostat and thereby double its carrying capacity and at the same time make current control easier and more accurate. In Fig. 1 is shown diagrammatically a slide rheostat with the additions necessary in order that both ends can be used.

The current ordinarily enters at the binding post A, passes through the resistance R and out at the binding post C through the slide CC'. As the slide

S_1 is moved towards A to increase the current, more and more of the resistance is cut out of the circuit and is not used. To change the rheostat so as to double its carrying capacity put on a second slide, S_2, a second binding post, B, at the end of the rheostat opposite A and a switch, K, so connected that when it is closed the two binding posts, A and B, are connected. To operate the rheostat proceed in the ordinary manner (switch K open) with the current entering at A passing through the resistance R, the slide S_1 and out at C. To increase the current move this slide towards A until it has passed over three fourths of the distance from B to A. To obtain a larger current move both slides to the center of the resistance R and close the switch K. The resistance will be about the same as it was with one slide and one-fourth of the resistance in use. The current will be divided at A and one half of it will enter at B and pass out at S_2, the other half entering at A and passing out at S_1. To increase the current move either slide S_1 towards A, slide S_2 towards E, or move the two slides farther apart.



Two such rheostats have been made in Nela Research Laboratories and used regularly for a year or more and found convenient to control a current of fifty to sixty amperes with a rheostat originally constructed to carry but thirty.

This plan can be carried a step further by introducing another switch K_1 as shown by the dotted line in Fig. 1 and by adding two more contacts.

NELA RESEARCH LABORATORIES, CLEVELAND, OHIO,
April, 1921.

A TRANSITION OR ADSORPTION LAYER THEORY OF THE E.M.F. OF THE VOLTAIC CELL.

BY RICHARD D. KLEEMAN.

A METAL plate immersed in a liquid or solution necessarily gives rise to a transition layer in the immediate vicinity of the plate in which the density of the liquid is different from that in the interior of the liquid, due to the nature and magnitude of the molecular forces to which the elements of the liquid are subjected, being different near the plate from what obtains at other parts. In the case of a solution this may give rise to a different density of the solute in the layer, which is known as adsorption. If the solute is an electrolyte the dissociation in the layer would therefore be different from that in the interior of the solution, and would vary from one part of the layer to the other. Due to the different rates of diffusion of the positive and negative ions an electric field would accordingly be set up across the layer. The formation of this field

would be attended by a charging up of the plate. Ultimately equilibrium of the ions in the solution would exist under the electric field due to the *charge on the plate*, and the field due to the *separated charges of opposite signs in the solutions*.

A difference of potential would accordingly exist between the interior of the metal plate and the remote side of the solution. The differential equations of this potential can be formed and are given in the paper. It is also proposed that the e.m.f. of a cell arises entirely in the foregoing manner. Various consequences that follow from this proposition are pointed out and discussed.

If the difference of potential of the *separated charges* in the solution is small in comparison with that due to the *charge on the plate*, as may occasionally be the case, we would be dealing with a case covered by Nernst's solution pressure theory of the e.m.f. of a cell. It appears therefore that the theory proposed by the author would explain the "mechanism" of Nernst's solution pressure in those cases where his theory is applicable. And in the cases where it cannot be applied without difficulties being introduced, as for example happens when the nature of each electrode is different from that of the deposit obtained on it on allowing an electric current to flow through the system, the theory proposed simply explains the e.m.f., and besides explains the change in the e.m.f. caused by the polarization of the electrodes.

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QUANTUM THEORY OF PHOTOGRAPHIC EXPOSURE.

BY LUDWIK SILBERSTEIN.

THE author assumes that the light impinging upon the photographic plate consists, either in part or entirely, of discrete light quanta, and that the necessary and sufficient condition for a silver halide grain to be "affected" by light, *i.e.*, to be made developable, is that it should be fully hit by and absorb a light quantum. The question is thus reduced to a problem in probabilities. For moderate numbers of grains and of light quanta the number of silver halide grains affected is represented by a harmonic series, which for large numbers of the former leads to an exponential formula, valid for each size (area)-class of grains separately. The exponent is proportional to the size of the grain and, for light quanta of non-negligible section, is a function of the wave-length showing a maximum. *Cæteris paribus*, the "speed" of a photographic plate is thus shown to increase with the size of the grain; at the same time the maximum sensibility shifts towards the red end of the spectrum. The available photographic data seem to corroborate characteristically some of the consequences of the theory. Other consequences, with all their quantitative details, are being subjected to special sensitometric, microscopic, and spectrophotometric tests now in progress in the Eastman Laboratory. Three sets of exposures gave a striking agreement with the formula.

THE PHYSICAL CONSTITUENTS OF THE ATMOSPHERE OF VENUS.

BY CHAS. E. ST. JOHN AND SETH B. NICHOLSON.

THE literature on planetary atmospheres is permeated with the assumption that the atmosphere of Venus is similar to our own, in particular as to the presence of oxygen and water vapor. This assumption rests upon spectrographic observations with low dispersion in which an increased intensity of the terrestrial lines was thought to be seen in spectra of Venus. Spectrograms of Venus with a dispersion of 3 Å. per mm. when the relative velocity was sufficient to separate lines due to atmospheric absorption in Venus from the corresponding terrestrial lines show, however, no trace of lines in the positions in which the Venus components should appear. From comparison with laboratory observations it is deduced that companions to the terrestrial lines should have been detected, if the light had penetrated a layer of oxygen on Venus equivalent in radial depth to 3 meters of oxygen under normal conditions.

In the depth penetrated in the planet's atmosphere there was then less than one five-hundredth part of the amount of oxygen in the earth's atmosphere.

As to water vapor it is deduced that if the solar beam had traversed, in and out, one millimeter of precipitable water, the water-vapor lines would have been doubled.

According to Jewell's observations the water vapor in the atmosphere over Baltimore is equivalent to 40 mm. of water. Moore gives it as about 50 mm. for the ordinary American climate.

MOUNT WILSON SOLAR OBSERVATORY.

THE SEPARATION OF MERCURY INTO ISOTOPES.

BY WILLIAM D. HARKINS AND R. S. MULLIKEN.

THE paper reports the details of the apparatus used in a separation of the isotopes of mercury amounting to 127 parts per million. It is found that the separation attained varies as the logarithm of the cut and as the square of the difference of atomic weight (when there are only two isotopes), and inversely as the mean atomic weight.

UNIVERSITY OF CHICAGO.

THE CRYSTAL STRUCTURE OF MERCURY.

BY L. W. MCKEEHAN AND P. P. CIOFFI.

THE crystal structure was determined by the "powder" method developed by A. W. Hull,[1] and with standard equipment for the use of molybdenum x-rays obtained from the General Electric Company. The low temperature required to keep the mercury frozen was obtained by boiling liquid air by an electric heater in a small vacuum flask and allowing the vapor to escape through

[1] PHYS. REV. (2), *10*, 661 (1917).

a glass tube in which the cylindrical sample was mounted axially. A temperature of about $-115°$ C. was thus maintained. To prevent the deposit of ice crystals on the air conduit it was made double walled with vacuum heat insulation. The sample itself consisted of a thin coat of minute mercury droplets condensed on the outer surface of a paraffin- or shellac-coated glass capillary tube mounted in metal bearings and provided at one end with a light screw propellor. The cooling air thus supplied the motive power for rotating the sample. Since much of the radiation utilized had to traverse six thicknesses of glass, the thinnest practicable walls were used and pyrex glass was chosen, further, to minimize absorption. Even so, exposures up to nearly thirty hours were required with 30–35 milliamperes through the x-ray tube, and the photographs are too faint for easy reproduction.

Preliminary trials, using the plots furnished with the apparatus[1] showed the best fit with a rhombohedral lattice with the axial ratio 1.94. It was assumed in the calculations that the agreement between the spacings of (111) and (110) planes was exact, which requires

$$\lambda = \cos^{-1}\tfrac{1}{3} = 70° - 31'.7,$$
$$C = \tfrac{1}{2}\sqrt{15} = 1.9365,$$

and gives a pattern of great simplicity. The tabulated values include all the

Miller Indices.	Theoretical Spacings.	Observed Spacings.		Relative Intensity Estimated.
		No. 1.	No. 2.	
	$a = 3.025$ $\lambda = \cos^{-1}(\frac{1}{3})$			
100	2.761	2.760	2.771	8
111	2.250	2.245	2.255	10
100				
$10\bar{1}$	1.747	1.748	1.750	6
$11\bar{1}$	1.476	—[2]	1.474	4
211				
210	1.381	1.382	1.379	2
100(2)				
221	1.235	1.255	1.235	2
$20\bar{1}$				
111(2)	1.127	1.125	—	1
110(2)				
$21\bar{1}$	1.083	1.085	—	1
$2\bar{1}\bar{1}$	1.008	—	1.035	1
311				
321	0.947	—	0.943	1
310				

[1] A. W. Hull and W. P. Davey, PHYS. REV. (2), *17*, 549 (1921).

[2] Bad spot on film too close to estimate position of line.

Rhombohedral System: $\lambda = 70° 31'.7$, $a = 3.025 \times 10^{-8}$ cm.,
Hexagonal System: $C = 1.9365$, $a = 3.493 \times 10^{-8}$ cm.
Atomic volume: 23.82×10^{-24} cm.^{3},

distinct lines on the two best photographs, and show excellent agreement with the assumed structure. The calculated density if one atom is associated with each cell (simple rhombohedral lattice) is 13.97 gm./cm.^{3} If the value of Mallet[1] for the density of solid mercury at its melting point, 14.193 gm./cm.^{3}, and that of Dewar[2] for its density in liquid air, 14.382 gm./cm.^{3}, are accepted, the density at $-115°$ C. should be about 14.29 gm./cm.^{3}, which differs from the value here determined by considerably more than its probable error, and may indicate that a closer packing of atoms can occur in large ingots than in microscopic droplets.

The other members of the group to which mercury belongs are magnesium, zinc, and cadmium, all of which form close packed hexagonal lattices, the axial ratio increasing from that appropriate to spheres, 1.624 in the case of magnesium[3] though 1.860 in the case of zinc,[4] to 1.89 in the case of cadmium.[4] The structure of mercury here found is not a close packing for spheroids, and is the first simple rhombohedral arrangement obtained for an elementary substance.

RESEARCH LABORATORIES OF THE
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[1] J. W. Mallet, Roy. Soc. Lond. Proc., *23*, 71 (1877).
[2] J. Dewar, Chem. News, *85*, 277 (1902).
[3] A. W. Hull, Nat. Acad. Sci. Proc., *3*, 470 (1917).
[4] A. W. Hull, PHYS. REV. (2), *17*, 571 (1921).